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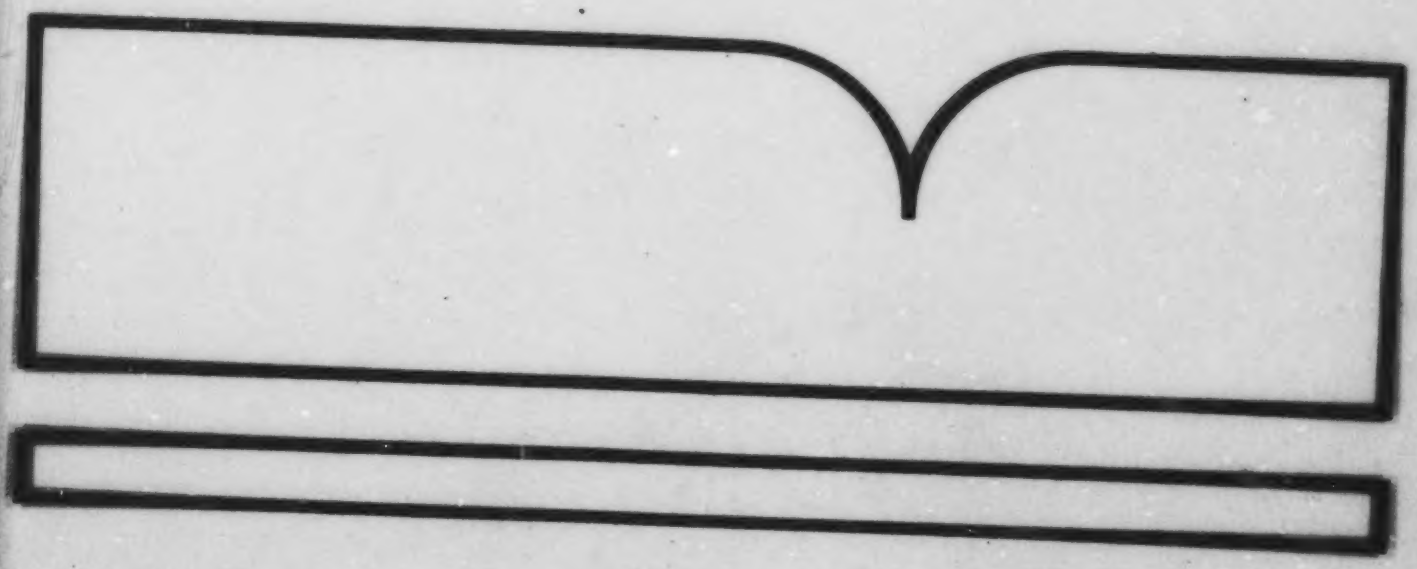
Technical and Economic Evaluation of Organic Acid Addition to a Commercial FGD System

Radian Corp., Austin, TX

Prepared for

Environmental Protection Agency
Research Triangle Park, NC

Apr 85



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TECHNICAL AND ECONOMIC EVALUATION OF ORGANIC ACID ADDITION TO A COMMERCIAL FGD SYSTEM

By

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The report summarizes the results of organic acid addition tests at a commercial FGD system. The tests were conducted at San Miguel Electric Cooperative's 410 MW lignite-fired Unit 1, outside Jourdanton, TX. During the program, several organic acid mixtures were tested over a range of operating conditions to determine if the use of organic acids would allow San Miguel to reduce FGD system operating costs. Based on the test results, a cost analysis indicated that the use of organic acid addition at San Miguel will result in a first-year cost savings of over $600,000. In terms of cumulative net present worth, the estimated savings over a 15-year period will be $7.2 million in 1984 dollars.

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ABSTRACT

This report summarizes the results of organic acid addition tests at a commercial FGD system. The tests were conducted at San Miguel Electric Cooperative's 410 MW lignite-fired Unit 1 located outside Jourdanton, Texas. During the program, several organic acid mixtures were tested over a range of operating conditions. The objective of these tests was to determine if the use of organic acids would allow San Miguel to reduce FGD system operating costs. Based on the test results, a cost analysis indicated that the use of organic acid addition at San Miguel will result in a first-year cost savings of over $600,000. In terms of cumulative net present worth, the estimated savings over a fifteen-year period will be $7.2 million in 1984 dollars.

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SECTION 1
SUMMARY

This section summarizes the results of a test program which characterized the technical and economic aspects of organic acid addition to a commercial FGD system. The program was sponsored by EPA's Industrial Environmental Research Laboratory at Research Triangle Park (IERL-RTP) in cooperation with San Miguel Electric Cooperative, Inc. Radian Corporation was responsible for providing San Miguel with engineering and analytical support during the test program. This report includes the results of an engineering analysis of the organic acid addition tests conducted at the San Miguel plant and a site-specific economic analysis which evaluates the cumulative net present worth of the organic acid addition options tested during the program.

Please note that this summary is a stand alone document. As a result, much of the information presented in this section is repeated in the main report which begins with Section 2: Introduction.

1.1 BACKGROUND

Many of the existing and planned FGD systems in the United States use limestone as an alkaline reagent to react with SO_2 and produce a calcium sulfite and/or sulfate waste sludge. Although this technology has been under development for nearly 15 years, many of the existing limestone systems have problems in meeting design levels of reagent utilization* and

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*Reagent utilization and stoichiometric ratio (S.R.) are both measures of the quantity of limestone used relative to the SO_2 removed in an FGD system. In this paper, S.R. = (moles $CaCO_3$ added) ÷ (moles SO_2 removed), and reagent utilization = 100 percent ÷ (S.R.).

SO_2 removal. One common problem is an inability to meet SO_2 emission regulations at low stoichiometric ratios (i.e., 1.1 or less). Often limestone FGD systems are forced to operate at stoichiometric ratios of 1.3 or more. Not only does this result in increased operating costs, but it can lead to other problems (e.g., mist eliminator pluggage) which may make it difficult to operate the FGD system. In some cases, even extremely high limestone stoichiometries (1.5 or greater) will not allow a utility to meet emission limits and, depending on specific SO_2 emission regulations, the boiler may have to be derated because of the inability of the FGD system to perform at design levels.

Most problems with poor SO_2 removal or poor limestone utilization are symptoms of poor mass transfer (both gas/liquid and solid/liquid) in the FGD system. Many of these problems can be corrected with equipment modifications but, for an operating FGD system, such modifications can prove quite costly. Another alternative is the use of an organic acid buffer to improve the mass transfer rate of SO_2 from the flue gas into the scrubber slurry.

Organic acids were identified as potentially attractive buffering agents for FGD systems more than 10 years ago [1]. With a constant slurry feed pH, use of an organic acid which buffers in the correct range can help maintain a higher average slurry pH in the absorber of an FGD system and therefore increase SO_2 removal. Organic acid buffers can also be used to maintain constant SO_2 removal efficiency at a lower pH. For FGD systems which can meet SO_2 emission regulations only at very high absorber feed pHs (i.e., high limestone stoichiometries), an organic acid buffer can be used to meet SO_2 emission limits at a lower pH and a consequently lower stoichiometry. Depending on the specific situation, the costs of organic acid addition may be more than offset by reduced limestone consumption, and a net reduction in costs can result.

EPA's Industrial Environmental Research Laboratory is responsible for conducting research to improve the performance and reliability of lime and

limestone FGD systems. Since 1977, EPA has studied the use of adipic acid* as a buffering agent for use in FGD systems. Initial tests with adipic acid at EPA's laboratories and in a pilot unit at Tennessee Valley Authority's Shawnee Power Plant showed promising results. Based upon those initial tests, EPA sponsored a full-scale demonstration of adipic acid addition to a FGD system at Springfield City Utilities' Southwest Power Plant. As part of the Springfield test program, a mixture of dibasic acids** (consisting of adipic, glutaric, and succinic acids) was also tested as a buffering agent. The results of these tests led to the permanent installation of a dibasic acid (DBA) addition system at the Springfield Plant [2].

In another EPA sponsored study, the costs of DBA addition were estimated for several operating FGD systems including San Miguel Electric Cooperative's 410 MW lignite fired Unit 1 located outside Jourdanton, Texas. For the San Miguel plant, the results of the economic analysis indicated that over a 15-year period, the cost of using DBA could range from an increase of $657,000 to a savings of $10,778,000 in terms of net present worth. This range in costs was a result of uncertainties in the DBA consumption rate, the estimated improvement in limestone utilization, and the SO_2 removal which could be achieved with DBA addition [3]. Because of the potential savings associated with DBA addition, San Miguel agreed to participate with EPA in a program to gather data on the technical and economic aspects of DBA use at the San Miguel plant.

1.2 OBJECTIVES AND APPROACH

The overall goal of the San Miguel test program was to expand the technical and economic data base on the use of organic acid in full-scale

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*Adipic acid is a dibasic organic acid which buffers in the 3 to 6 pH range.

**This dibasic acid mixture is a by-product of adipic acid manufacture.

FGD systems. The approach used to meet this objective involved testing of several organic acid additivies at San Miguel Electrical Cooperative's Unit 1, a 410 MW lignite fired boiler. The Unit 1 FGD system consists of four 33 percent capacity modules with one typically used as a spare. Each module includes a venturi-type quench tower for saturation of the flue gas and a tray-type absorber where most of the SO_2 removal occurs. During the test program, the three on-line modules were all operated with organic acid addition. Test durations ranged from 2 days to 1 week, and for each test samples were collected to permit completion of DBA material balances around the FGD system and measurement of representative limestone ($CaCO_3$) utilizations in the system. Process data were collected to quantify FGD operation including the overall SO_2 emission rate, the flue gas bypass rate, and typical operating pHs in the system.

For each test, the general operating goals were to maintain the plant SO_2 emissions at or below 1.2 $lb/10^6$ Btu*, the absorber pHs at 5.8, the quencher pHs at 5.4, the gas flow through the modules at or below the design level of 500,000 acfm/module, and the organic acid buffer capacity at a relatively constant level. Of these goals, maintaining SO_2 emissions below 1.2 $lb/10^6$ Btu took precedence. At times this resulted in deviation from one or more of the other test goals.

1.3 PLANT DESCRIPTION

San Miguel Cooperative's Unit 1 is a 410 MW lignite fired boiler located in Atascosa County outside of Jourdanton, Texas. The plant is a mine-mouth facility firing a high-sulfur (about 2 percent), high ash (about 20 percent), low heating value (about 5600 Btu/lb) Texas lignite. Because of the poor fuel quality, the plant requires operation of an air quality control system consisting of an electrostatic precipitator for particulate

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*It is EPA policy to report measurements in SI units. However, because of convention in the electric utility industry, this report uses British engineering units. A table of conversion factors is attached.

collection, followed by a Babcock & Wilcox designed FGD system for SO_2 removal. The FGD system was designed to meet a Federal and State SO_2 emission limit of 1.2 $lb/10^6$ Btu which corresponds to about 85 percent SO_2 removal at 2700 ppm SO_2 inlet concentration.

The San Miguel Unit 1 FGD system consists of four quench-absorber modules, two 115-ft diameter thickeners, thickener underflow and overflow storage tanks, a limestone feed preparation system, and a solids dewatering and disposal system.

Figure 1-1 is a schematic of the FGD system which shows one of four identical absorber modules. Two boiler ID fans exhaust flue gas to a common plenum which supplies the scrubber modules. Any of the modules can be isolated from the flue gas path by closing inlet and outlet dampers. In addition, there is a flue gas bypass which can be used if SO_2 emissions drop below the 1.2 $lb/10^6$ Btu limit. Since flue gas exiting the scrubber is reheated, hot flue gas bypass reduces the load on the reheat system and, therefore, increases overall plant efficiency.

Flue gas which enters the absorbers (about 1,500,000 acfm) first passes down through a venturi-type quench tower where the gas contacts sprays of recirculating slurry is saturated with water, and some SO_2 removal occurs. The gas then turns 180° and passes up through a perforated tray type absorber where it is contacted with a recirculating slurry of calcium sulfite/sulfate and limestone. There, the majority of the SO_2 removal occurs. The flue gas then leaves the absorbers and passes through a 2-stage Chevron type mist eliminator before entering a reheat chamber common to all four modules. The scrubbed flue gas is mixed with bypassed flue gas and with ambient air which has been heated to 400°F by steam coils. After the flue gas is reheated, it enters the stack and is discharged to the atmosphere.

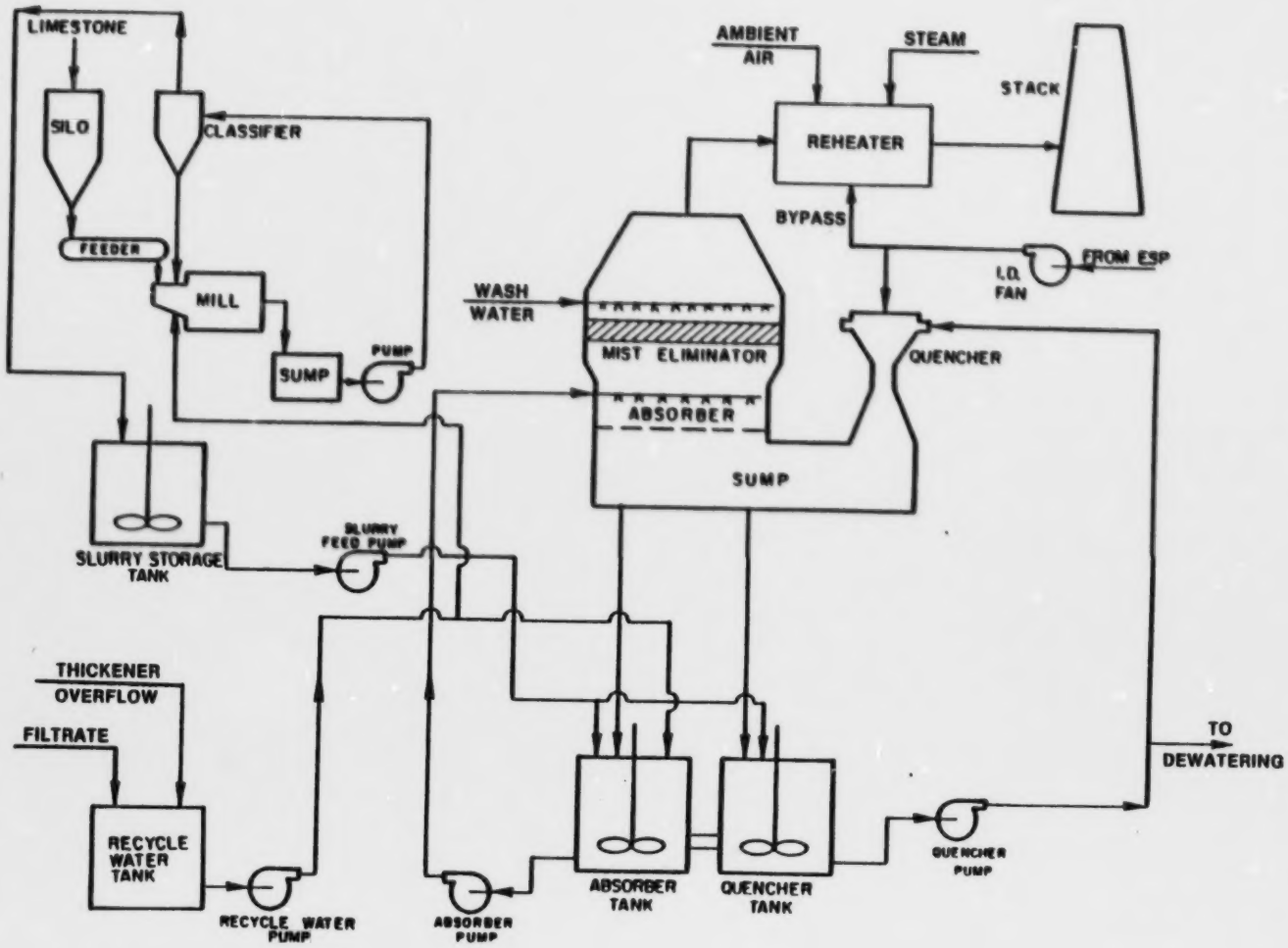

Figure 1-1. San Miguel FGD System.

1.4 TEST PROGRAM

San Miguel became interested in organic acid addition to the Unit 1 FGD system when an economic analysis showed that use of organic acids could result in a net reduction in FGD system operating costs. Prior to the use of DBA at the San Miguel plant, the FGD system operated with very high limestone stoichiometries (i.e., greater than 1.4) which resulted in high limestone reagent costs. San Miguel was also interested in DBA addition because it offered the possibility of alleviating some of their operating problems, including mist eliminator pluggage.

The key factors affecting the economics of organic acid addition to the San Miguel FGD system were:

- The quantity of organic acid consumed in the FGD system at different organic acid concentrations in the circulating slurry,
- The limestone stoichiometry which could be achieved at different levels of organic acid addition to the system, and
- The quantity of flue gas which could be bypassed at different levels of organic acid addition to the system.

The initial test program for San Miguel was structured to address these key economic considerations.

Originally, the San Miguel test program was scheduled to evaluate two organic acid sources at three different concentrations in the recirculating slurry. The acid sources were:

- A DBA solution supplied by DuPont Petrochemicals of Victoria, Texas, and

- An organic acid solution supplied by Badische Corporation of Freeport, Texas.

The initial phase of the test program using the DuPont supplied DBA was carried out as scheduled. However, the tests using the Badische acid were terminated after the first test because of severe foaming in the absorber and quench recirculation tanks which made it very difficult to operate the FGD system. After this test, the program was modified to include tests not originally scheduled. The new tests included:

- Testing of an organic acid byproduct stream consisting primarily of maleic acid which was supplied by Badische Corporation, and

- Testing of manganese addition (as $MnSO_4$) to the FGD system to reduce organic acid consumption.

The San Miguel organic acid addition program consisted of nine tests including a baseline test prior to the start of DBA addition to the system. Table 1-1 presents the actual and planned operating conditions for each organic acid addition test. As shown, actual operating conditions (represented by test averages) differ slightly from the planned operating conditions.

The most significant difference between planned and actual test conditions was for the Badische EP-501 test where the buffer capacity was 25 percent of the planned level. This deviation is a result of several factors, including very high consumption rates measured for EP-501 and several late deliveries of the EP-501 material which caused the organic acid feed to be temporarily discontinued.

Table 1-2 presents typical compositions for the three organic acid mixtures tested at San Miguel. The compositions shown are from suppliers' analyses.

TABLE 1-1. SAN MIGUEL ORGANIC ACID TEST CONDITIONS

Test ID	Organic Acid Tested	Buffer Capacity (ppm)		Absorber pH		Quench pH		SO_2 Emissions $lb/10^6$ Btu		Mn Concentration (ppm)	
		Planned	Actual	Planned	Actual	Planned	Actual	Planned	Actual	Planned	Actual
DuPont 1	DuPont: DBA	500	632	5.80	5.83	5.40	5.48	1.15	1.02	NA	1
DuPont 2	DuPont: DBA	1000	1415	5.80	5.77	5.40	5.47	1.15	0.98	NA	1
DuPont 3	DuPont: DBA	2000	2018	5.80	5.82	5.40	5.47	1.15	0.77	NA	1
Badische 1	Badische: EP-306	500	461	5.80	5.79	5.40	5.69	1.15	1.00	NA	1
Badische 2	Badische: EP-501	500	125	5.80	6.05	5.40	5.86	1.15	1.07	NA	1
Mn 1	DuPont: DBA	500	643	5.80	5.90	5.40	5.56	1.15	1.07	15	6
Mn 2	DuPont: DBA	500	574	5.80	5.90	5.40	5.57	1.15	1.02	30	10
Mn 3	DuPont: DBA	500	629	5.80	5.86	5.40	5.64	1.15	1.10	15	10

TABLE 1-2. TYPICAL COMPOSITIONS FOR THE ORGANIC ACID MIXTURES TESTED AT SAN MIGUEL

	Mixture		
	DuPont DBA	Badische EP-306	Badische EP-501
Wt. % acids as delivered	50	25	20
Component (% of total acids)			
Adipic	15	45	--
Succinic	25	3	--
Glutaric	60	5	--
Hydroxy Caproic	--	35	--
Maleic	--	--	80
Others	--	2	20

1.5 RESULTS

The discussion of the results of the San Miguel organic acid addition tests is organized into four areas:

- Performance results,
- Operation results,
- Additive effects, and
- Economic results.

Each of these areas is summarized below.

Performance Results

The San Miguel test program examined different organic acids over a range of operating conditions. Table 1-3 summarizes many of the key measures of process performance for these tests. The data in Table 1-3 are useful in estimating the effects of various additives, and they can also be used to compare the San Miguel results with those of other programs. In terms of process costs, two of the most significant items included in Table 1-3 are organic acid consumption and limestone utilization. These are discussed in detail below.

Organic Acid Consumption--

Organic acid consumption is one of the most significant factors which can affect the costs of DBA addition to an FGD system. Previous tests have shown that organic acid consumption in an FGD system can be a function of several factors including buffer capacity* (which for a given acid or acid mixture is proportional to concentration), sulfite oxidation, acid composition, manganese concentration, pH, etc. For any of these factors that can be controlled, it is important to quantify how they affect organic acid consumption and also how they affect limestone utilization and bypass rate.

Figure 1-2 presents the organic acid consumption rates for the San Miguel tests as a function of buffer capacity. The figure also includes a curve which is a regression fit of the DuPont DBA test results. It should be noted that the consumption rates in Figure 2 represent the total organic acid loss rate in the San Miguel system including:

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*Buffer capacity is a relative measure of the ability of an organic acid or acid mixture to buffer over the pH range 6 to 3. For this study, buffer capacities are reported relative to the buffer capacity of adipic acid.

TABLE 1-3. SAN MIGUEL TEST SUMMARY

ITEM	TEST ID							
	DuPont 1	DuPont 2	DuPont 3	Badische 1	Badische 2	Mn 1	Mn 2	Mn 3
BUFFER CAPACITY (ppm)	632	1415	2018	461	125	643	574	629
BUFFER TYPE	DuPont DBA	DuPont DBA	DuPont DBA	EP-306	EP-501	DuPont DBA	DuPont DBA	DuPont DBA
MANGANESE CONC. (ppm)	1	1	1	1	1	6.9	10.8	10.8
ORGANIC ACID CONSUMPTION								
a. lb/hr	293	535	582	196	241	326	271	321
b. lb/ton SO2	18.0	34.4	35.2	12.9	17.1	28.7	24.4	29.7
INLET SO2 (lb/MMBtus)								
a. Coal Analysis	7.41	7.41	7.41	7.07	7.07	5.19	5.19	5.19
b. SO2 Monitors	7.68	6.45	7.55	7.20	6.48	6.08	5.70	5.59
SO2 EMISSIONS (lb/MMBtu)	1.02	0.98	0.77	1.00	1.07	1.07	1.02	1.10
SO2 REMOVAL - MODULES (%)								
a. Coal Analysis	91.1	94.1	95.8	87.5	87.8	84.0	86.0	83.6
b. SO2 Monitors	90.8	94.1	96.1	82.4	86.5	90.3	91.4	94.1
SO2 REMOVAL - SYSTEM (%)								
a. Coal Analysis	86.2	86.8	89.7	85.9	84.9	79.4	80.4	78.8
b. SO2 Monitors	86.7	84.8	89.9	86.1	83.5	82.4	82.1	80.3
SO2 REMOVED (tons/hr)	16.3	15.6	16.6	15.2	14.1	11.5	11.2	11.0
LIMESTONE UTILIZATION (%)								
a. Absorbers	85.9	86.3	74.0	65.7	79.1	79.3	82.1	82.3
b. Quenchers	85.0	89.4	91.3	82.7	84.8	87.8	92.6	88.4
OPERATING pHs								
a. Absorbers	5.83	5.77	5.82	5.79	6.05	5.90	5.90	5.86
b. Quenchers	5.48	5.47	5.47	5.69	5.86	5.56	5.57	5.64
GAS FLOWS (wet Mscfm)*								
a. Modules	1296	1266	1268	1358	1301	1295	1295	1300
b. Bypass	73.5	106.9	86.7	26.5	29.5	75.3	91.4	78.4
c. Reheat	109.9	57.1	192.0	182.7	192.5	143.0	131.7	167.1
MAXIMUM BYPASS (wet Mscfm)*								
a. Coal Analysis	89.4	130.5	150.5	48.5	50.9	84.6	115.8	78.9
b. SO2 Monitors	77.3	162.7	150.4	-39.0	53.5	127.4	162.2	201.9
SULFITE OXIDATION (%)								
a. Absorbers	24.9	25.6	26.1	24.2	26.3	26.9	29.0	35.9
b. Quenchers	24.9	25.3	22.0	25.2	25.2	24.3	27.2	33.1

* Mscfm = 1000 standard (60°F, 29.92 inHg) cubic feet per minute.

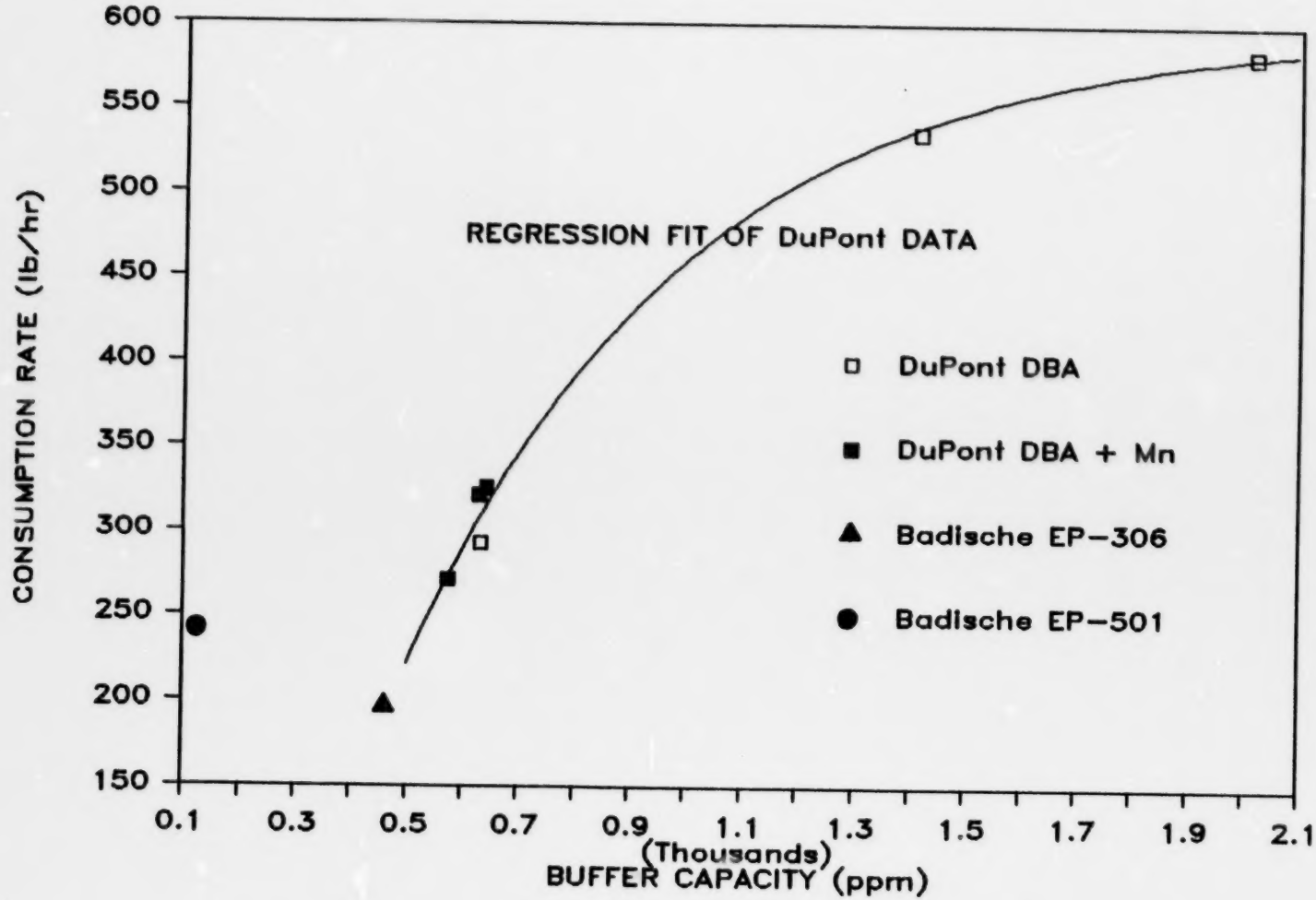

Figure 1-2. Organic Acid Consumption vs Buffer Capacity for all Organic Acids Tested.

- Losses due to chemical degradation of the organic acids,

- Losses due to precipitation or co-precipitation of the organic acids with the calcium-sulfur salts produced in the system, and

- Losses due to organic acids present in process liquor entrained with the waste solids.

No attempt was made to differentiate or individually quantify these mechanisms.

Figure 1-2 illustrates several interesting results. First, it indicates that the DuPont DBA consumption rate increases at a less-than-linear rate over the range of buffer concentrations tested. In other words, a doubling of the DBA buffer capacity does not double the DBA consumption rate. This result is consistent with laboratory results for adipic acid which showed that consumption is proportional to acid concentration to the 0.55 power[4].

Another important result illustrated in Figure 1-2 is the effect of manganese on the DBA consumption rates. As shown, the DuPont tests with manganese do not differ appreciably from the comparable DuPont test without manganese. This is in contrast to results reported by other investigators. Previous studies have shown that manganese can reduce the chemical degradation part of adipic acid losses to near zero[4].

The reasons for the differences between the San Miguel manganese tests and previous tests are not clear. It may be that differences between pure adipic acid and the DBA acid mixture tested at San Miguel can account for the fact that manganese does not appear to have a significant effect on the DBA consumption rate. Another possibility is that the operating conditions during the manganese tests at San Miguel were outside the range in which manganese affects the organic acid degradation mechanism (e.g., the Mn concentrations were too low). Also, it may be that chemical degradation

represents only a small faction of the overall organic acid consumption rate at San Miguel. In any event, no benefit from manganese addition was observed at the conditions tested at San Miguel.

A third important result illustrated by Figure 1-2 is the relative consumption rates of the three organic acid additives tested at San Miguel. As shown, the two organic acid mixtures supplied by Badishe have significantly different consumption rates relative to each other. The additive EP-306, which is a mixture consisting primarily of mono-basic hydroxy caproic acid and dibasic adipic acid, shows a consumption rate which appears to be consistent with the consumption rates for the DuPont DBA mixture. However, EP-501 additive, which is a mixture consisting primarily of dibasic maleic acid, has a high consumption rate relative to the buffer capacity provided. Figure 1-2 shows that, although the buffer capacity for the EP-501 test is about 20 percent of that in the lowest buffer capacity DuPont additive test, the consumption rate is about 80 percent. Also, the consumption rate for the maleic acid test is actually higher than that for the EP-306 test while the buffer capacity is less than one-third of that provided by EP-306.

Limestone Utilization--

Limestone utilization is another factor which has a significant impact on the costs associated with organic acid addition. The major driving force for use of an organic acid additive at San Miguel was the potential for reducing limestone consumption by an amount which would more than offset the cost of the organic acid additive and the capital charges for an organic acid feed system. Some additional benefits from increased limestone utilization were also expected (e.g., reduced mist eliminator pluggage), but were not a significant factor in the initial evaluation of the costs of organic acid addition.

Table 1-4 summarizes the limestone utilization data collected during the test program at San Miguel. It includes data from baseline conditions (prior to organic acid addition) and each of the organic acid tests. Data are presented for both the quench and absorber loops, although the

TABLE 1-4. SAN MIGUEL TEST AVERAGES - OXIDATION, UTILIZATION, AND pH

Test ID	Absorber			Quencher		
	Oxidation	Utilization	pH	Oxidation	Utilization	pH
Baseline	20.0%	66.9%	6.16	18.9%	70.0%	6.09
DuPont 1	24.9%	85.9%	5.93	24.9%	85.0%	5.53
DuPont 2	25.6%	86.3%	5.87	25.3%	89.4%	5.49
DuPont 3	26.1%	74.0%	6.04	22.0%	91.3%	5.58
Badische	24.2%	65.7%	6.05	25.2%	82.7%	5.79
Maleic	26.3%	79.1%	6.16	25.2%	84.8%	5.84
Manganese 1	26.9%	79.3%	5.87	24.3%	87.8%	5.67
Manganese 2	29.0%	82.1%	5.85	27.2%	92.6%	5.64
Manganese 3	35.9%	82.3%	5.89	33.1%	88.4%	5.65

measurement of the quench solids represents overall limestone utilization since it is these solids which are ultimately discharged from the FGD system. As shown, the baseline utilization measured at San Miguel averaged 70 percent, while the organic acid addition tests had utilizations ranging from 83 percent to nearly 93 percent. The measured utilizations for the organic acid addition tests are based on samples collected from operating quench loops each day during the tests. This represents a substantial improvement which was accompanied by a reduction in process costs.

Operation Results

In addition to the quantitative results of the San Miguel organic acid tests, there were some qualitative observations made during the test program

which may be of interest to utilities considering an organic acid additive to enhance the performance of a limestone FGD system. The discussion which follows summarizes those observations. Areas which are addressed include:

- pH meter maintenance and operation,
- Thickener operation,
- Absorber and mist eliminator pluggage,
- Foaming in the recirculation tanks,
- FGD system water balance, and
- Corrosion of the organic acid feed system.

A general discussion of each of these areas is provided along with comments relating to specific test conditions where appropriate.

pH Meter Maintenance and Operation--

Prior to the use of organic acid addition at San Miguel, pH was not a critical operating variable in the FGD system. Limestone addition was controlled by the pH feedback loop, but this was often overridden by the need to meet the 1.2 $lb/10^6$ Btu SO_2 emission limit. In such cases, limestone was added to the FGD system regardless of the pH. After the start of the organic acid addition tests, accurate pH readings became more important. It was necessary to control the quench loop pH at 5.4 to obtain the maximum cost benefit from the use of organic acid in the FGD system. Only by operating at this lower pH was it possible to reduce limestone stoichiometry and, therefore, reduce operating costs.

San Miguel has a regular pH meter maintenance program which includes calibration of the pH monitors once a shift and a check to ensure that there is adequate sample flow past the pH electrodes. Typical problems include pH meter drift, sample line pluggage, and breakage of pH electrodes. Of these problems, the last two are more serious. Plugged sample lines cause the pH meter to read high, while broken electrodes can cause erratic readings.

Because San Miguel had a pH meter maintenance program in place, system pH measurements were generally accurate. As a result, the pH meter maintenance schedule did not require any changes once organic acids were added to the FGD system. However, in many plants where the pH meters receive less attention, an improved maintenance schedule will be needed to accrue the full cost savings associated with organic acid addition; and in some cases, an improved pH monitoring system may even be needed.

Thickener Operation--

One noticeable change in FGD system operation which occurred once organic acids were added to the San Miguel system was in the performance of the thickeners. Prior to the start of organic acid addition, the thickeners were often "cloudy", and they operated with only one clear sample port*. In addition, a flocculent was used to aid in setting of fine particles which were responsible for the "cloudy" appearance. Shortly after the start of organic acid addition to the system, thickener operation improved dramatically. Three clear ports in the thickener became common, and the addition rate of flocculent was reduced.

It is believed that the improvement in thickener operation is an indirect result of organic acid addition to the FGD system. The direct cause is the reduction in operating pHs which corresponds to a reduction in the amount of excess limestone in the system. At lower excess limestone levels in the FGD system, there is a reduced load on the thickener which would tend to improve operation. In addition, lowering the excess limestone would be expected to significantly reduce the number of very fine particles in the system. This should also help thickener operation.

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*Sample taps are located in the side of each thickener at regular intervals. The number of "clear ports" is the number of taps from the top of the thickener which discharge clear liquor when sampled.

The improvement in thickener operation discussed above was observed during all but one of the organic acid addition tests. The one exception occurred during the tests with the Badische DBA additive (EP-306). During these tests, foam from the quench tank was carried to the center well of the thickeners. The foaming action tended to cause the center well to overflow into the thickener and, as a consequence, the cloudiness in the thickeners returned. This problem was one reason why the planned tests with EP-306 were cancelled.

Absorber and Mist Eliminator Pluggage--

A number of changes in FGD system operation were made possible once organic acid addition was initiated at San Miguel. As a result of those changes, several improvements in operation were observed. One of the most significant improvements was virtual elimination of scaling and plugging of the absorber trays and mist eliminators. This resulted in a significant reduction in the maintenance effort required to keep the FGD system running.

Prior to organic acid use, San Miguel routinely had a full time (40 hr/wk), 5 to 10 person crew cleaning absorber trays and mist eliminator passages in the spare module. However, after the start of the organic acid tests, module inspections revealed little or no scale in the absorbers or mist eliminator, and the cleaning effort was substantially reduced. The biggest problem which remained was pluggage of spray nozzles in the absorbers with deposits which formed and sloughed off the absorber and quencher walls.

The reduction of absorber tray and mist eliminator plugging at San Miguel is attributed to the changes which were made possible by organic acid addition. Two of the most significant changes were:

- Operating at an absorber pH of 5.8 - At this pH there is less excess limestone in the recirculating slurry than during previous operation at a pH of 6.3 to 6.5.

- Operation at lower absorber gas velocities - Before organic acid addition, removal levels in the FGD system were just at the level required by regulations, and little flue gas bypass of the quench-absorber modules was possible. However, with organic acids, it became possible to bypass up to 10 percent of the flue gas around the scrubber modules. This lowered the gas velocity through the modules and would be expected to reduce carryover to the mist eliminators.

Foaming in the Recirculation Tanks--

One problem which has been observed with the use of some organic acid mixtures in an FGD system is foaming. Foaming is caused by soap-like impurities in organic acid mixtures, and it can be a significant operating problem. During the tests at San Miguel, foaming was obseved under all conditions, but the severity of the foaming problem varied. During the tests with the DuPont supplied DBA, foaming was first observed at a buffer capacity of about 600 ppm. At this level of buffer capacity, the recirculating tank levels were reduced from 19 to 17 ft to provide 5 ft of freeboard in the tank and thereby prevent the tanks from foaming over. At higher levels of DuPont DBA, the foaming became more severe and, at a buffer capacity of 2,000 ppm, the recirculation tanks periodically overflowed. However, no other adverse effects of foaming were observed during this test.

Following the DuPont DBA tests, the FGD system was purged of organic acid by discontinuing addition of the DBA. Tests were then initiated using the organic acid material supplied by Badische Corporation (EP-306). During the first of three scheduled tests using this material, the foaming in the recirculation tanks was more severe at a buffer capacity of around 500 ppm than during the DuPont DBA tests at a 2,000 ppm buffer capacity. In response to this problem, San Miguel lowered the recirculatin tank levels an additional 2 ft (to 15 ft) which provided a total of 7 ft of freeboard. Even at this tank level, the Badische material caused the tanks to foam-over almost continuously.

FGD System Water Balance--

One minor effect of the changes made possible by organic acid addition was a reduction in the quantity of water consumed by the FGD system. At the lower limestone stoichiometries made possible with the use of organic acids, the quantity of waste generated by the FGD system was reduced by approximately 17 percent by weight. Assuming that the weight fraction of water in the solids from the vacuum filter is relatively constant, a decrease in the total mass of solids results in a slight decrease in the total water consumed by the FGD system (i.e., evaporated water plus water associated with the waste solids). For San Miguel this change was estimated to be about 5 percent of the FGD system's total water requirement, and it did not have a significant impact on the system water balance. For other systems, the change in the system water balance may be more significant.

Corrosion of the Organic Acid Feed System--

San Miguel had a serious problem with corrosion of the organic acid feed system during the initial months of operation. Corrosion has occurred in all areas of the feed system including the tank heater (which failed after only 20 days of operation), lines, valves, and the tank itself. This problem has proved quite costly, increasing San Miguel's capital investment for the organic acid system by nearly 50 percent.

The DBA feed system at San Miguel was constructed of 304 SS. This type of steel has been used by Badische and DuPont for handling and storing DBA, and they have reported no problems. In addition, other FGD systems have used 304 SS successfully for handling DBA.

It appears, then, that the problems at San Miguel are site-specific. It is believed that San Miguel's corrosion problems are a result of mixing FGD process liquor and cooling tower blowdown (CTB) water with organic acids in the storage tank. An analysis of pipe samples from San Miguel's organic acid feed system has shown severe pit corrosion of the material. This corrosion was attributed to chloride attack of the metal under the acidic

conditions (pH = 3.0) present in the DBA feed system. No chloride measurements were made of the DBA material itself, but an analysis of the FGD process liquor and CTB water showed chloride levels between 5000 and 9000 ppm.

Since the feed system corrosion became severe, San Miguel has replaced the stainless steel feed lines with PVC and has repaired the feed tank twice. They have also avoided adding water to the organic acid feed. This has minimized the current problem, but the initial corrosion problem obviously resulted in an additional capital expense. Utilities considering the use of organic acids should benefit from this experience at San Miguel. The solution is to either avoid addition of chloride containing water to the organic acid feed or use a chloride resistent material such as fiberglass or PVC.

Additive Effects

Of the three organic acid additives tested, only the DuPont DBA was examined over a range of conditions. The Badische supplied acids (EP-306 and EP-501) were tested at only one level. The results of these tests permit two general comparisons. The DuPont material provided good performance over the range of conditions tested. However, foaming did begin to be a problem at a buffer capacity of 2,000 ppm. The Badische material EP-306 was tested only at a buffer capacity of about 500 ppm; but at this level, foaming was more severe than that observed for the DuPont material at 2,000 ppm. Because of the severe foaming, planned tests using EP-306 at higher buffer capacities were cancelled. The test with the Badische additive EP-501 did not exhibit any unusual foaming problems.

In terms of acid consumption rates, the DuPont material exhibited a less-than-linear increase in consumption as a function of buffer capacity. The Badische additive EP-306 appeared to have a consumption rate similar to the DuPont material. The additive EP-501 had a consumption rate which appeared to be significantly higher than that of either the DuPont material

or the EP-306 additive. Comparisons of the consumption rates of these additives should be made with caution, however, because the tests with the Badische additives were outside the range of buffer capacities examined for the DuPont additive.

Economic Results

The overall measure of how organic acid additives affected operation of San Miguel's FGD system is the reduction in process operating costs which resulted. One method of evaluating the savings is to estimate the cumulative net present worth (CNPW) of the organic acid addition project. Table 1-5 summarizes the results of three, 15-year CNPW analyses which compare the

TABLE 1-5. FIFTEEN-YEAR CUMULATIVE NET PRESENT WORTH FOR THE THREE ADDITIVES TESTED AT SAN MIGUEL

	Estimated Savings (costs) in $1000S Acid/Buffer Capacity		
Cost Component*	DuPont DBA/ 600 ppm	EP-306/ 460 ppm	EP-501/ 125 ppm
Capital Investment	(215)	(215)	(215)
Organic Acid	(6093)	(3395)	(5054)
Limestone Reagent	6939	5949	4562
Limestone Grinding	1306	1120	859
Sludge Disposal	2523	2163	1659
Maintenance	752	---	---
Dewatering	353	303	232
Bypass Credit	1650	914	914
Total	7215	6839	2957

*All costs in mid-1984 dollars.

three organic acid additives tested at San Miguel. Component contributions to the CNPW are also shown. The CNPW represents the estimated savings in mid-1984 dollars over a 15-year period of organic acid use in the San Miguel FGD system. As shown, the projected savings for the three additives range from nearly $3 million for the Badische EP-501 additive to $7.2 million for the DuPont DBA additive. This indicates that San Miguel will realize a very significant savings from the use of an organic acid additive. At current prices, the DuPont additive is the most attractive offering a 6 percent greater savings than the Badische EP-306 additive. Also, operation with the DuPont DBA provides additional benefits such as reduced absorber and mist eliminator pluggage and improved thickener operation.

As shown in Table 1-5, the only cost items included in the CNPW analysis are the capital investments associated with the organic acid addition system and the continuing costs for the organic acid additive. The capital investment shown represents the initial investment in 1983, the costs incurred for repairs due to corrosion, and planned expenditures to improve the organic acid addition system in 1984. Since most of the capital costs have already been incurred, these will not be affected by the projected CNPW. However, a significant change in the delivered price of DBA or limestone could have a proportionally significant impact (either positive or negative) on the present worth of the organic acid addition project at San Miguel. This should be considered in using the San Miguel results to evaluate organic acid addition for other applications.

Of the items in Table 1-5 which represent cost savings, most are related to the improvement in limestone utilization including:

- Limestone Reagent Cost Savings - This represents the improvement in limestone utilization which resulted from operation at lower quencher pHs. Baseline limestone consumption was estimated on 70 percent utilization.

- Limestone Grinding Cost Savings - The reduction in limestone grinding costs was calculated based on the estimated reduction in annual reagent consumption, costs for electricity, and the operating characteristics of the limestone grinding circuit. In addition, a reduction in the quantity of balls required to maintain the ball mill charge was estimated.

- Sludge Disposal Savings - Reducing the excess limestone produces a proportional reduction in the quantity of waste sludge generated by the FGD system. Savings associated with sludge disposal were estimated based on the limestone savings, operating characteristics of the dewatering area, and San Miguel's costs for waste disposal.

- Dewatering Cost Savings - A reduction in the mass of waste generated also reduces the load on the vacuum filtration system. This cost savings represents the reduction in power consumption which results from reduced operating time for the dewatering system.

There are two other items not related to limestone consumption which contribute to the projected cost savings at San Miguel:

- Reduced Absorber Maintenance - The use of DuPont DBA at a buffer capacity of 600 ppm allowed the San Miguel FGD system to operate at conditions which reduced the tendency of the absorbers and mist eliminators to plug. San Miguel estimates that this has reduced the FGD system maintenance by at least 50 percent. The maintenance cost savings were not included for the two Badische additives because, when these additives were tested, the FGD system was operated at conditions which did result in plugging in the absorbers and mist eliminators.

- Bypass Credit - The use of organic acids in the San Miguel FGD system permitted varying amounts of flue gas to be bypassed around the modules. If more gas was bypassed, less reheat was required and a cost savings resulted. These savings were included in the economic analysis by estimating bypass rates for each organic acid addition test.

1.6 CONCLUSIONS

Several major conclusions can be drawn based on the results of the San Miguel test program:

- The use of organic acids in the San Miguel FGD system resulted in a significant improvement in process operation and a very substantial cost savings. The maximum estimated savings was over $600,000 in first year savings. This translates to $7.2 million in 1984 dollars over a 15-year period. These maximum savings were calculated for DuPont DBA additive added to attain an average buffer capacity of 600 ppm.

- Savings for the Badische additive, EP-306, were only slightly lower than for the DuPont material. However, the EP-306 additive was not "penalized" for the foaming problem, which made operation at a buffer capacity of more than 500 ppm very difficult. In fact, foaming was so severe that this test was terminated, and subsequent tests planned for higher buffer capacities were cancelled.

- Savings for the Badische additive, EP-501, were substantially less than for either the DuPont DBA or EP-306. This was due to a very high consumption rate of EP-501, relative to the buffer capacity provided.

- The key to realizing the savings associated with organic acid addition at San Miguel was a significant reduction in limestone

stoichiometry in the FGD system. Limestone stoichiometry was reduced by reducing operating pHs in the quench and absorber recirculating loops.

- Another benefit of operating at a lower absorber pH was a reduction in the pluggage of absorber trays and mist eliminator passages.

- Use of organic acids at San Miguel made some flue gas bypass possible. This contributed to the projected cost savings by reducing the requirement for reheat steam.

- Organic acid concentrations were not found to have a direct effect on the limestone utilization of the system. Only by allowing operation at lower pHs did the organic acids affect utilization.

- Tests with manganese added to the FGD system showed no effect on the organic acid consumption rate. This is in contrast to previous test results.

In conclusion, substantial benefits resulted from the use of organic acids in the San Miguel FGD system. Significant cost savings will be realized by San Miguel due to changes in FGD operating conditions made possible by organic acid use. Also, improvement in FGD operation (such as reduced absorber and mist eliminator pluggage) was an indirect result of organic acid use at San Miguel. Because of these benefits, San Miguel plans to continue organic acid addition to the FGD system.

1.7 REFERENCES

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SECTION 2
INTRODUCTION

This report presents the results of a test program which characterized the technical and economic aspects of organic acid addition to a commercial FGD system. The program was sponsored by EPA's Industrial Environmental Research Laboratory at Research Triangle Park (IERL-RTP) in cooperation with San Miguel Electricl Cooperative, Inc. Radian Corporation prepared this report and was responsible for providing San Miguel with engineering and analytical support during the test program. This report includes the results of an engineering analysis of the organic acid addition tests conducted at the San Miguel plant and a site-specific economic analysis which evaluates the cumulative net present worth of the organic acid addition options tested during the program.

2.1 BACKGROUND

Many of the existing and planned FGD systems in the United States use limestone as an alkaline reagent to react with SO_2 and produce a calcium sulfite and/or sulfate waste sludge. Although this technology has been under development for nearly 15 years, many of the existing limestone systems have problems in meeting design levels of reagent utilization* or SO_2 removal. One common problem is an inability to meet SO_2 emission regulations at low stoichiometric ratios* (i.e., 1.1 or less). Often limestone FGD systems are forced to operate at stoichiometric ratios of 1.3 or more.

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*Reagent utilization and stoichiometric ratio (S.R.) are both measures of the quantity of limestone used relative to the SO_2 removed in an FGD system. In this report, S.R. = (moles $CaCO_3$ added) (moles SO_2 removed) and reagent utilization = 100 percent ÷ (S.R.).

Not only does this result in increased operating costs, but it can lead to other problems (e.g., mist eliminator pluggage) which may make it difficult to even operate the FGD system. In some cases even extremely high limestone stoichiometries (1.5 or greater) will not allow a utility to meet emission limits and, depending on specific SO_2 emission regulations, the boiler may have to be derated because of the inability of the FGD system to perform at design levels. Obviously this type of problem can be quite costly to a utiity, especially if the plant is a new base-loaded unit.

There are a variety of reasons why an FGD system may not perform at design levels. Some of the common ones includes:

- Poor Limestone Grind - Studies have shown that limestone grind can have a significant impact on SO_2 removal efficiency at otherwise constant operating conditions[1]. When compared to a finely ground limestone (95% past 325 mesh), a poor grind (e.g., less than 80% past 325 mesh) can result in reduced SO_2 removal efficiency at constant stoichiometric ratio or reduced limestone utilization at constant removal efficiency.

- Unreactive Limestone - Different limestones have been shown to dissolve at different rates under identical scrubber operating conditions [2]. An unreactive limestone could have the same net effect on scrubber performance as poor limestone grind.

- Poor Gas/Liquid Mass Transfer - Many limestone FGD systems employ spray tower designs to help minimize plugging. Spray towers, however, are relatively poor gas/liquid contactors and are more susceptible to gas/liquid distribution problems. This type of problem can result in poor SO_2 removal efficiencies or excessively high limestone stoichiometric ratios.

These examples illustrate some possible reasons an FGD system may not meet its design SO_2 removal level. There are others. Most of the problems with poor removal or poor limestone utilization are symptoms of poor mass transfer (both gas/liquid and solid/liquid) in the FGD system. Many of these problems can be corrected with equipment modifications but for an operating FGD system, such modifications can prove quite costly. Another alternative is the use of an organic acid buffer to improve the mass transfer rate of SO_2 from the flue gas into the scrubber slurry in an FGD system.

Organic acids were identified as potentially attractive buffering agents for FGD systems more than 10 years ago [3]. With a constant slurry feed pH, use of an organic acid which buffers in the correct range can help maintain a higher average slurry pH in the absorber of an FGD system and therefore increase SO_2 removal. Organic acid buffers can also be used to maintain constant SO_2 removal efficiency at a lower pH. For FGD systems which can only meet SO_2 emission regulations at very high absorber feed pHs (i.e., high limestone stoichiometries), an organic acid buffer can be used to meet SO_2 emission limits at a lower pH and a consequently lower stoichiometry. Depending on the specific situation, the costs of organic acid addition may be more than offset by reduced limestone consumption and a net cost savings can result.

EPA's Industrial Environmental Research Laboratory is responsible for conducting research to improve the performance and reliability of lime and limestone FGD systems. Since 1977, EPA has studied the use of adipic acid* as a buffering agent for use in FGD systems. Initial tests with adipic acid at EPA's laboratories and in a pilot unit at Tennessee Valley Authority's Shawnee Power Plant showed promising results. Based upon those initial tests, EPA sponsored a full-scale demonstration of adipic acid addition to a limestone FGD system at Springfield City Utilities' Southwest Power Plant. As part of the Springfield Test Program, a dibasic acid mixture (which is an

*Adipic acid is a dibasic organic acid which buffers in the 6 to 3 pH range.

adipic acid byproduct) was also tested as a buffering agent. The results of these tests led to the permanent installation of a dibasic acid (DBA) addition system at the Springfield Plant [4]

The results of the tests at Springfield and a subsequent EPRI-sponsored study at the Duck Creek Station of Central Illinois Lighting Company (CILCo) [1] have shown the use of organic acid buffers (specifically DBA) to be a cost-effective means of meeting SO_2 emission regulations with a limestone FGD system. However, the DBA consumption rates measured at Springfield and CILCO have differed significantly from laboratory and pilot plant data. This has led to uncertainty in projecting the DBA consumption rates for other utilities who may be considering organic acid addition as a means of enhancing FGD system performance. As a result of this uncertainty, EPA continued to examine the economics of organic acid addition and to pursue opportunities to expand the technical and economic data base on the use of DBA in FGD systems.

In another EPA sponsored study, the costs of DBA addition were estimated for several operating FGD systems including San Miguel Electric Cooperative's 410 MW lignite fired Unit 1 located outside Jourdanton, Texas. For the San Miguel plant, the results of the economic analysis indicated that over a 15-year period, cost of using DBA could range from an increase of $657,000 to a savings of $10,778,000 in terms of net present worth. This range in costs was a result of uncertainties in both the DBA consumption rate and the estimated reduction in limestone stoichiometry which could be achieved with DBA addition [5]. Because of the potential savings associated with DBA addition, San Miguel agreed to participate with EPA in a program to gather data on the technical and economic aspects of DBA use at the San Miguel plant.

2.2 OBJECTIVES AND APPROACH

The overall goal of the San Miguel test program was to expand the technical and economic data base on the use of organic acid in full-scale

FGD systems. The approach used to meet this objective involved testing of several organic acid additivies at San Miguel Electrical Cooperative's Unit 1, a 410 MW lignite fired boiler. Unit 1's FGD system consists of four 33 percent capacity modules with one typically used as a spare. Each module includes a venturi-type quench tower for saturation of the flue gas and a tray-type absorber where most of the SO_2 removal occurs. During the test program, the three on-line modules were all operated with organic acid addition.

The program conducted at San Miguel included a baseline test and a total of eight tests with organic acids. The baseline test was simply a characterization of the San Miguel FGD system prior to the start of organic acid addition. The organic acid tests covered a range of operating conditions including different acid types and concentrations and the use of manganese additive in an attempt to modify the acid degradation rate.

2.2.1 Test Objectives

Some more specific objectives of the San Miguel test program included:

- Quantifying the consumption rates of two different DBA additives at several levels of buffer capacity in the scrubber feed slurry. Organic acid mixtures were obtained from DuPont Petrochemicals and from Badische Corporation for testing. After the start of the test program a third additive, consisting primarily of maleic acid, was also tested.

- Quantifying changes in limetone stoichiometry which resulted from modified system operation made possible with organic acid addition.

- Completing a site-specific economic analysis of the costs and savings for organic acid addition at the San Miguel plant.

- Quantifying the effects of manganese addition on the organic acid consumption rates in the FGD system.

2.2.2 Test Approach

The approach used to meet the San Miguel test objectives involved collection of process samples and process data which characterized FGD system operation during the organic acid addition tests. Test durations ranged from 2 days to 1 week and for each test, samples were collected to permit completion of organic acid material balances around the FGD system and measurement of representative $CaCO_3$ utilizations in the system. Process data were collected to quantify FGD operation including the overall SO_2 emission rate, the flue gas bypass rate, and typical operating pHs in the system.

For each test, the general operating goals were to maintain the plant SO_2 emissions at or below 1.2 $lb/10^6$ Btu, the absorber pHs at 5.8, the quencher pHs at 5.4, the gas flow through the modules at or below design levels (500 macfm/module), and the organic acid buffer capacity at a relatively constant level. Of these goals, maintaining SO_2 emissions below 1.2 $lb/10^6$ Btu took precedence. At times this resulted in deviation from one or more of the other test goals.

2.3 REPORT ORGANIZATION

This report presents the results of the organic acid addition test program at San Miguel's Unit 1 FGD system. Section 1 is a summary of the test program which highlights the significant technical and economic results. Section 2 is an introduction to a more detailed presentation of the program. Section 3 presents a description of the San Miguel FGD system, while Section 4 presents details of the test program. Section 5 presents test results and Section 6 contains an economic analysis of the various organic acid addition options tested during the program. Section 7 presents

conclusions based on the results of the test program and a discussion of data quality is included in Appendix A.

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SECTION 3
THE SAN MIGUEL PLANT

3.1 PLANT DESCRIPTION

San Miguel Electric Cooperative's Unit 1 is a 410 MW lignite fired boiler located in Atascosa County outside of Jourdanton, Texas. The plant is a mine-mouth facility firing a high-sulfur (about 2 percent), high ash (about 20 percent), low heating value (about 5600 Btu/lb) Texas lignite. The fuel quality is so poor that it may be the lowest rank coal which has been considered for a large power station in the United States [1]. A typical fuel analysis is shown in Table 3-1.

TABLE 3-1. TYPICAL FUEL ANALYSIS FOR SAN MIGUEL GENERATING STATION

COMPONENT	PERCENT
Carbon	39.1
Hydrogen	3.4
Nitrogen	0.7
Oxygen	9.5
Sulfur	1.8
Ash	19.4
Moisture	26.0

The San Miguel plant began commercial operation in January 1982 and it is the only facility operated by the San Miguel Electric Cooperative. It is a base-loaded unit which normally operates at or above the 410 MW design

output 24 hours a day. Thus far the plant has operated about 300 days per year.

Because of the poor fuel quality, the plant requires operation of an air quality control system consisting of ESP followed by a Babcock & Wilcox designed FGD system. The FGD system was designed to meet a Federal and State SO_2 emission limit of 1.2 lb/10^6 Btu which corresponds to about 85 percent SO_2 removal at 2700 ppm SO_2 inlet concentration.

3.2 FGD SYSTEM DESCRIPTION

The San Miguel Unit 1 FGD system consists of four quench-absorber modules, two 115-foot diameter thickeners, thickener underflow and overflow storage tanks, a limestone feed preparation system, and a solids dewatering and disposal system. The limestone feed preparation system includes limestone unloading facilities, 375,000 ft^3 of raw limestone storage, limestone conveyors, and a limestone grinding circuit. The grinding circuit includes a 26 ft. x 12 ft. diameter ballmill, fifteen 4 inch diameter Krebs hydrocyclones for limestone classification, and a 150,000 gal limestone slurry storage tank. The dewatering system includes three 18 ft. x 12 ft. diameter rotary vacuum filters and two pug mills for mixing the filtered solids with fly ash prior to final disposal.

3.3 FLUE GAS FLOW

Figure 3-1 is a schematic of the San Miguel FGD system. Two axial-flow boiler ID fans exhaust flue gas to a common plenum which supplies the four scrubber modules. Any of the four modules can be isolated from the flue gas path by closing module inlet and outlet dampers. In addition, there is a flue gas bypass which can be used if module SO_2 removals result in SO_2 emissions below the 1.2 lb/10^6 Btu limit. Since flue gas exiting the scrubber is reheated, hot flue gas bypass reduces the load on the reheat system and therefore increases overall plant efficiency.

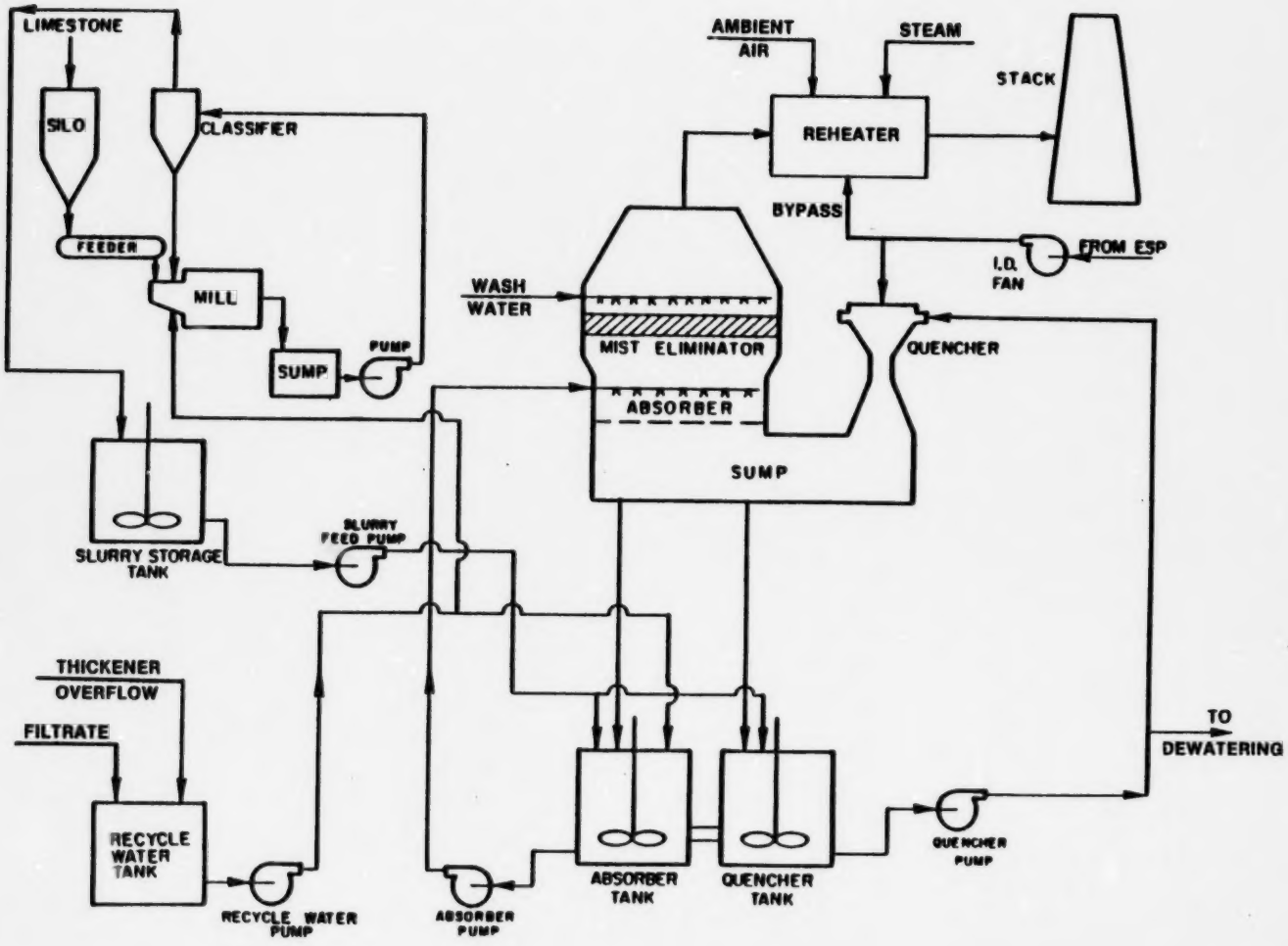

Figure 3-1. San Miguel FGD System.

Flue gas which enters the absorbers (about 1,500,000 acfm) first passes down through a venturi-type quench tower where the gas contacts sprays of recirculating slurry is saturated with water, and some SO_2 removal occurs. The gas then turns 180° and passes up through a perforated tray type absorber where the majority of the SO_2 removal occurs.

The flue gas leaves the absorbers and passes through a 2-stage Chevron type mist eliminator before entering a reheat chamber common to all four modules. There, the scrubbed flue gas is mixed with bypassed flue gas and with ambient air which has been heated to 400°F by steam coils. Steam used for reheat is extracted from the turbine at 180 psia and 720°F which results in a reduction of overall plant efficiency. At the start of the organic acid test program at San Miguel, the flue gas was reheated to 160°F but in December 1983, during some unusually cold weather, the reheat temperature was raised to 175°F where it is currently set.

After the flue gas is reheated, it enters the stack and is discharged to the atmosphere. The stack is equipped with extractive SO_2 and CO_2 monitors which the plant personnel use to determine compliance with the 1.2 $lb/10^6$ Btu SO_2 emission regulation. This continuous emissions monitoring system (CEMS) has been certified according to EPA procedures outlined in the Federal Register.

3.4 SLURRY FLOW

Limestone reagent for the FGD system is ground and slurried in the ball mill, classified in a hydroclone circuit, and discharged to a storage tank. Slurry from storage is then fed to the absorber and/or quench recirculation tanks to maintain pH in these tanks at a set level. The limestone feed and pH control system is designed so the pH in the absorber and quench loops can be controlled independently (within certain limits). Overall slurry flow in the system is such that it cascades from the absorber recirculation tank to the quench tank. Slurry from the quench loop is continuously blown down to the thickeners for dewatering and eventual disposal.

Prior to the organic acid addition tests at San Miguel, the FGD system was operated with the recirculating slurry in both the quench and absorber loops at a pH in the range of 6.2 to 6.5. Limestone was added only to the absorber but the excess in the absorber slurry was enough to maintain the recirculating slurry in the quench loop at or near the same pH. Operation in this manner resulted in overall limestone stoichiometries between 1.4 and 1.5 which correspond to utilizations of 65 to 70 percent. After the organic acid addition tests were initiated, it became possible to operate the absorber slurry loop at a pH of 5.8. This resulted in low pHs (less than 5.0) in the quench loop. Under these conditions, limestone was added directly to the quench tank to maintain the recirculating pH at 5.4 in order to provide some SO_2 removal in the quench tower.

Slurry withdrawn from the quench loop is sent to the thickeners at about 17 percent solids. There it is dewatered to about 35 percent and the underflow is sent to a storage tank which feeds three rotary vacuum filters. The vacuum filters dewater the slurry to about 50 percent solids. Filtrate and the overflow from the thickeners are both sent to a hold tank which returns the clarified liquor to the absorbers and quenchers. The thickener overflow/filtrate liquor is also used in the limestone grinding circuit to slurry the limestone. Solids are discharged from the vacuum filter at about 50 percent moisture and then mixed with fly ash to form a 90 percent solids mixture which is returned to the lignite mine for disposal.

Overall, the San Miguel FGD system is operated with a closed water loop. Fresh water is input in the slurry recirculation pump seals and the vacuum pump seals. Thickener overflow is used for slurrying the limestone and the mist eliminator wash water is a mixture of ash pond water and cooling tower blowdown. The combination of fresh and plant water added to the system is roughly equal to the losses from evaporation and the loss with the dewatered sludge.

3.5 ORGANIC ACID FEED SYSTEM

San Miguel installed a permanent organic acid feed system prior to the test program. This feed system included a 30,000 gallon 304 SS insulated and heated storage tank, a stainless steel, positive displacement feed pump and insulated 304 stainless steel lines and rotameters to supply organic acid to the absorber recirculation tanks of each module. This system did not include any automatic controls; all adjustments to the acid feed rate were made manually and rotameters were checked periodically to ensure flows were at the desired level. The initial system design included an electric, stainless steel immersion heater to maintain the organic acid temperature around 120°F. This was necessary to prevent acids from precipitating from solution and subsequently plugging the feed system. The organic acids as received at the plant contained up to 80 weight percent acid. As a result, the feed system also included a dilution system which mixed plant water with as-received acid to lower the concentration of organic acids in the tank and consequently lower the temperature at which acid would precipitate.

On initial start-up, the acid feed system worked well and the rotameters required little adjustment to maintain constant flow to the absorber tanks. However, the feed system began to experience corrosion problems after about 2 to 3 weeks of operation. Initially, the electric heater shorted out due to corrosion of the heater element sheath. Then, valves and supply lines began to leak due to corrosion. Eventually, the leakage became so severe that the feed system had to be replaced.

Subsequent analysis of pipe samples from San Miguel revealed severe pit corrosion which was attributed to chloride attack of the stainless steel. The apparent source of chloride and cause of the corrision was FGD process water which was used to dilute the organic acid mixtures. Apparently, the low pH and high chloride levels (which were not measured) in the diluted acid caused the corrosion problem.

After failure of the 304 stainless steel pipe, San Miguel replaced the original system with insulated PVC material; and instead of feeding organic acid to individual modules, the system was configured to feed acid to the thickener overflow tank. The modified feed system worked without mechnical problems but it was less responsive to required changes in acid concentrations in any one module. In addition, due to some peculiarities of the FGD system design, feeding organic acid through the thickener overflow tank caused a stratification of acid concentrations in the FGD system. The stratification was due to different make-up water demands by each module with Module A having the greatest make-up requirement (and therefore the highest acid feed rate) and Module D having the lowest (with the lowest acid feed rate). Different modules were found to have different make-up water demands because of the way the mist eliminator wash water header operated. Module D is closest to the main water header and has the highest wash water pressure. This translates to the greatest water flow during washing and a consequently lower demand for make-up water from the thickener overflow tank.

Obviously, the modified organic acid feed system was not an optimum design, but it represented a quick and inexpensive alternative for the corrosion plagued stainless steel system. The lines which were run to the thickener overflow tank were much shorter than original lines and they required only one feed point rather than the original four. It should be noted that this feed system appeared to work well under steady-state operating conditions. However, it may not be suitable to respond to severe transient operations (e.g., large changes in inlet SO_2 concentration) due to the lag time between acid addition to the thickener overflow tank and addition of thickener overflow to the absorber.

3.6 REFERENCES

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SECTION 4
ORGANIC ACID ADDITION TEST PROGRAM

4.1 GENERAL DISCUSSION

San Miguel became interested in organic acid addition to the Unit 1 FGD system when an economic analysis showed the potential for a net reduction in FGD system operating costs. Prior to the use of organic acid at the San Miguel plant, the FGD system operated with very high limestone stoichiometries (i.e., greater than 1.4) which resulted in high limestone reagent costs. Even under those operating conditions, all the flue gas from the unit had to be processed in the FGD system to meet the 1.2 lb $SO_2/10^6$ Btu emission limit. This resulted in the reheat system being used to reheat all the flue gas from the boiler since little flue gas bypass was possible. San Miguel was also interested in DBA addition because it offered the possibility of alleviating some of their operating problems including mist eliminator pluggage.

The key factors affecting the preliminary economic analysis of organic acid addition to the San Miguel FGD system were:

- The quantity of acid consumed in the FGD system at different organic acid concentrations in the circulating slurry;
- The limestone stoichiometry which could be achieved at different levels of organic acid addition to the system; and
- The quantity of flue gas which could be bypassed at different levels of organic acid addition to the system.

The initial test program for San Miguel was structured to address these key economic considerations.

Originally, the San Miguel organic acid addition test program was scheduled to evaluate two organic acid mixtures at three different concentrations in the recirculating slurry. The acid mixtures were:

- A DBA solution supplied by DuPont Petrochemicals of Victoria, Texas, and

- A mixture of hydroxycaproic and adipic acids supplied by Badische Corporation of Freeport, Texas.

The initial phase of this test program using the DuPont supplied DBA was carried out as scheduled. However, the tests using the Badische acid were terminated after the first test because of severe foaming in the absorber and quench recirculation tanks (this is discussed in more detail in Section 5 - Test Results) which made it very difficult to operate the FGD system. After this test, the program was modified to include tests not originally scheduled. The new tests included:

- Testing of an organic acid byproduct stream consisting primarily of maleic acid which was supplied by Badische Corporation. Maleic acid was included for testing because on a weight-of-acid basis it is competitively priced with DBA.

- Testing of manganese addition (as $MnSO_4$) to the FGD system to reduce organic acid consumption. Manganese was tested because analysis of slurry samples from San Miguel showed very low levels (about 1 ppm) while studies have shown that at slightly higher concentrations (10 to 30 ppm), manganese can be effective in inhibiting organic acid degradation in an FGD system.

The test program at San Miguel began in December 1983 with the DuPont acid test and was completed in March 1984 with the manganese addition tests.

4.2 ACTUAL TEST CONDITIONS

The San Miguel organic acid addition program consisted of 9 tests including a baseline test prior to the start of organic acid addition to the system. Table 4-1 presents the actual and planned operating conditions for each organic acid addition test. As shown, actual operating conditions (represented by test averages) differ slightly from the planned operating conditions. The reasons for these differences and the significance of each of the operating variables are summarized in the following discussion.

4.2.1 Buffer Capacity

Buffer capacity of the recirculating slurry is a measure of the quantity of organic acid present in the slurry. It is determined by titrating a known volume of slurry from pH 6.0 to pH 3.0 and recording the quantity of titrant used. The result of the titration is related to a "standard" buffer capacity value for adipic acid and the buffer capacity values are reported as "equivalent ppm of adipic acid." This means that buffer capacity is an absolute measure of a slurry's ability to buffer in the pH 3 to 6 range but not a quantitative measure of the mass of organic acid present in solution. The relationship between buffer capacity and the mass of organic acid present depends on the actual acids in solution and the molecular weight and disassociation constants (pK_a) of those acids.

Table 4-2 presents the composition and the calculated relative buffer capacities for the three organic acid mixtures tested at San Miguel. The buffer capacities shown are estimated relative to adipic acid (also shown) and are for 1 gram of each acid mixture dissolved in 1 liter of water. The estimates in Table 4-2 are based on equilibrium concentrations and assume the activity of each acid is equal to its concentration in solution. These estimates indicate that, depending on the specific acid or mixture of acids

TABLE 4-1. SAN MIGUEL ORGANIC ACID TEST CONDITIONS

Organic Acid Tested	Buffer Capacity (ppm)		Absorber pH		Quench pH		SO_2 Emissions ($lb/10^6$ Btu)		Mn Concentration (ppm)	
	Planned	Actual	Planned	Actual	Planned	Actual	Planned	Actual	Planned	Actual
DuPont : DBA	500	632	5.80	5.83	5.40	5.48	1.15	1.02	NA	1
DuPont : DBA	1000	1415	5.80	5.77	5.40	5.47	1.15	0.98	NA	1
DuPont : DBA	2000	2018	5.80	5.82	5.40	5.47	1.15	0.77	NA	1
Badische : EP-306	500	461	5.80	5.79	5.40	5.69	1.15	1.00	NA	1
Badische : EP501	500	125	5.80	6.05	5.40	5.86	1.15	1.07	NA	1
DuPont : DBA	500	643	5.80	5.90	5.40	5.56	1.15	1.07	15	6
DuPont : DBA	500	574	5.80	5.90	5.40	5.57	1.15	1.02	30	10
DuPont : DBA	500	629	5.80	5.86	5.40	5.64	1.15	1.10	15	10

TABLE 4-2. COMPOSITIONS AND RELATIVE BUFFER CAPACITIES FOR THE ORGANIC ACIDS TESTED AT SAN MIGUEL

Acid Type	Adipic 100%	DuPont DBA	Badische EP-306	Badische EP-501
Mass (gm/1)	1	1	1	1
Conc (mm/1)	6.85	7.66	8.19	8.14
% Adipic	100	15	45	
% Succinic		25	3	
%Glutaric		60	5	
% H-Caproic			35	
% Maleic				80
% Phthalic				12
% Benzoic				4
% Citranoic				4
Total PPM As Adipic =	1000	1082	761	658

present, equal weights of acid do not provide equal buffer capacities. In fact, the 3 organic acid additives tested at San Miguel have esimated buffer capacities ranging from the Badische maleic mixture which has a buffer capacity of 68 percent of adipic acid to the DuPont DBA which has a buffer capacity of 108 percent of adipic acid. Please note that these estimates do not account for degradation or precipitation and so they are not indicative of the costs or consumption rates associated with use of any of these acids. Rather, they indicate that the buffer capacity measurement does not quantify actual acid concentration but does quantify the buffer capacity of a solution over the pH range 6 to 3.

Buffer capacity in the San Miguel system was controlled by adjusting the rate of organic acid addition based on analyses of buffer capacity in the absorber and quench recirculation loops. The primary control goal was to maintain buffer capacity at a constant level during each test and the secondary goal was to maintain the buffer capacity at a specified level. As evident from the test summary in Table 4-1, buffer capacities were not held at planned levels. This was due to several factors including the time required to analyze samples and adjust the organic acid feed rate and problems with timely delivery of the acid materials. These problems also made it difficult to maintain buffer capacities at a constant level during the tests.

4.2.2 Absorber and Quencher pHs

The principal benefit of organic acid buffer in the San Miguel FGD system was that it allowed the system to meet the 1.2 lb $SO_2/10^6$ Btu emission limit while operating with lower pHs in the circulating slurry. Prior to the start of the test program, the FGD system typically operated with absorber and quench loop pHs in the range of 6.3 to 6.5. After the start of organic acid addition, however, these pHs were reduced to 5.8 in the absorber and 5.4 in the quench loop. This reduction in operating pH provided San Miguel with several benefits; the primary one being a reduction in operating costs due to reduced limestone usage at the lower pHs. This result and others are discussed in more detail in Section 5 of this report.

During the organic acid addition tests, absorber and quencher pHs were controlled by a feedback system which added limestone to any tank on demand. Process pH measurements were made continuously by pH monitors which are located in a sidestream of the main quench and absorber recirculation loops. These pH monitors had a tendency to drift and the sample lines would plug. Consequently, San Miguel operating personnel checked sample flows and calibrated the on-line pH meters once a shift. This resulted in good pH control at the 5.4 and 5.8 setpoints although there were still some incidents where pH control would drift from the setpoints. Also, since the overriding

consideration in operating the FGD system was to meet the 1.2 $lb/10^6$ Btu emission limit, there were some cases where the operating pH was raised to prevent the plant from exceeding the emission limit. Causes for these excursions varied but could generally be attributed to lack of organic acid feed due to feed system problems of a missed or late delivery or a sudden increase in the inlet SO_2 concentration due to variations in coal quality. The pH setpoint increases occurred most often at low organic acid concentrations. During testing at the higher organic acid levels, plant operators simply adjusted the amount of flue gas bypass to scrub more flue gas if the SO_2 emission rate approached 1.2 $lb/10^6$ Btu.

4.2.3 SO_2 Emission Rate

As mentioned earlier, maintaining SO_2 emissions at or below the 1.2 $lb/10^6$ Btu limit was the overriding concern in operating the San Miguel FGD system. At times this caused deviations from planned test conditions. During the organic acid addition tests, most of the conflict between test conditions and actual operation occurred at low organic acid buffer capacities (about 500 ppm) where the system was just able to meet the emission limit at the pH levels of 5.4 and 5.8. SO_2 Emission rates are monitored continuously at San Miguel using an extractive monitoring system comprised of a pulsed fluorescence SO_2 monitor and an infrared CO_2 monitor. Signals from these monitors are input into the plant computer and output in the boiler and FGD system control rooms as $lb/10^6$ Btu. Plant personnel use this output to adjust the FGD system operation to meet the SO_2 emission limit.

During the organic acid addition tests, there were three primary means of adjusting system operation to meet the emission limits including:

- Operating pHs,
- Flue gas bypass, and
- Organic acid addition rate.

At the start of the test program, the acid addition rate was adjusted to determine what buffer capacity was needed to meet the emission limit at pHs of 5.4 and 5.8 in the quench and absorber with little or no flue gas bypass. This was selected as a minimum organic acid buffer capacity and was intended to serve as a baseline for each of the acids tested. If excursions occurred during this test, the only response possible was for the plant personnel to raise the operating pHs. They did this on several occasions.

During the tests at higher organic acid buffer capacities, the principal means of controlling SO_2 emissions was to adjust the flue gas bypass dampers so more or less flue gas was scrubbed. This tended to maintain SO_2 emission at or below 1.1 $lb/10^6$ Btu although during the tests at very high buffer capacities, the emission rates were substantially lower averaging less than 0.8 lb $SO_2/10^6$ Btu during one test. For the most part, plant personnel did not adjust the organic acid addition rate to respond to changes in emissions.

4.2.4 Manganese Concentration

Previous studies [1,2] have shown that the level of manganese in solution in a scrubber slurry can affect the rate of degradation of organic acids in the FGD system. Manganese is a catalyst for SO_3 oxidation in the system and it is believed that by modifying the oxidation reaction path, manganese also modifies the rate of degradation of organic acids.

After the initial tests at San Miguel, the DuPont DBA consumption rates were compared with results from the tests at Springfield City Utilities' Southwest plant. This comparison showed that DBA losses at San Miguel were 30 to 50 percent higher than the Springfield losses when adjusted to equivalent conditions. A subsequent analysis of slurry samples from San Miguel indicated that the level of manganese in solution was approximately 1 ppm. This is below the 10 to 30 ppm level which has been shown to inhibit organic acid degradation and the 15 ppm level found at Springfield. Because the

potential existed to substantially reduce acid costs with addition of manganese, several tests were conducted to investigate this possibility. In these tests, manganese (as $MnSO_4$) was added to the limestone in the ball mill and eventually fed to the scrubber. Manganese was added at rates calculated to produce 15 and 30 ppm during two tests, but actual concentrations were 6 and 11 ppm. Subsequent analysis of solids from the system indicated that some of the manganese had precipitated. The form of the precipitate was not determined.

During these tests, no control was actually exercised over the manganese concentration. An addition rate (in bags $MnSO_4$ per shift) was selected and used for each test. Actual levels of manganese were then determined by subsequent analysis.

4.2.5 Summary

The preceding discussion has presented some of the principal independent operating variables examined during the San Miguel test program. The response of dependent variables and general operating results are presented in Section 5 of this report.

4.3 PROCESS DATA COLLECTION

During each of the organic acid tests, data were collected to permit characterization of the operation of the FGD system. Much of these data are routinely collected by San Miguel and as such required no changes for the test program. A few items such as organic acid addition rates and flue gas bypass damper settings were added to the operator's logs for these tests. One item which was added to the computer for the organic acid tests was a 5-point DuPont SO_2 monitor which sampled the common inlet and the outlet of each of the four absorbers. This monitor was not operated by the plant prior to the test program, but it was made operational for the tests.

Table 4-3 presents a complete list of process data collected during the San Miguel tests. This table also indicates if the data were collected on a continuous basis by the plant computer or if the data were recorded on a periodic basis by the FGD system operators.

TABLE 4-3. PROCESS DATA COLLECTED DURING THE TEST PROGRAM

Measurement	Frequency
pH	H
Gas Flow	C
Inlet SO_2	C
Module Outlet SO_2	C
Stack SO_2	C
Gas Temperatures	C
Bypass Opening	H
DBA Flows	H
Coal Analyses	D
Unit Load	C

H = Hourly, C - Continously, D - Daily

4.4 SAMPLING AND ANALYSIS

As part of the organic acid addition test program, Radian provided San Miguel with sampling and analysis support. The sampling and analysis program was designed to quantify the costs and savings which resulted from organic acid addition to the San Miguel system. It was also designed to track changes in chemistry in the FGD system. Specific areas addressed by the sampling and analysis program included:

- Collection and analysis of process samples to permit completion of an organic acid material balance around the FGD system--This involved determining the total organic acid (as measured by buffer capacity) in all tanks, thickeners, etc. at the start and end of each test. These measurements were then used to calculate the accumulation (either positive or negative) of buffer capacity during a test. The accumulation was then subtracted from the total buffer added to determine the net consumption rate during each test.

- Collection and analysis of samples to quantify limestone stoichiometry during the test program--Emphasis was placed on measuring limestone utilization in the quench tanks since this represents the material eventually discharged from the system as waste and it also provides a more instantaneous measure of utilization. Overall utilization could also be measured in the thickener underflow or the cake from the vacuum filter but because of the long solid phase residence times in the dewatering system it is difficult to correlate these data with absorber and quencher operating conditions during non-steady-state operation. Measurements of limestone utilization in the absorber tanks were also made. These measurements document the reduction in excess limestone in the absorber relative to the levels measured prior to organic acid addition.

- Collection and analysis of samples to quantify sulfite oxidation in the system before and during the organic acid addition test program--Samples from both the absorber and quench were collected and analyzed. These samples indicate how operating conditions affected sulfite oxidation and were intended to provide guidance in case scaling problems were observed in the FGD system.

- Collection and analysis of samples to quantify operating buffer levels during each test--These samples were used to adjust acid feed rates to meet test conditions and to help maintain a relatively constant buffer capacity during each test.

Table 4-4 presents a complete summary of the sampling and analysis program for an individual test. As shown, some samples were collected once or twice per test. Others were collected every day for the duration of a test.

TABLE 4-4. SAMPLING AND ANALYSIS SCHEDULE FOR A TYPICAL ORGANIC ACID TEST

Sample Location	Slurry		Liquid Phase	Solid Phase			
	pH	temp	DBA	$CO_3^=$	$SO_3^=$	$SO_4^=$	Inerts
Absorbers	D	D	D	E	E	E	E
Quenchers	D	D	D	D	E	E	E
Thickener Overflow	S,E	S,E	S,E	-	-	-	-
Thickener Underflow	S,E	S,E	S.E	-	-	-	-
Limestone Feed Tank	S,E	S,E	S,E	-	-	-	-
Filter Feed Tank	S,E	S,E	S,E	-	-	-	-
Recycle Water Tank	S,E	S,E	S,E				

D = once per day during a test

S = start of test

E = end of test

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SECTION 5
TEST RESULTS

This section summarizes the results of the organic acid addition tests conducted at the San Miguel Unit 1 FGD system. The results are divided into three categories: performance results, operation results, and additive effects. The performance results summarize data and analyses which quantify the performance of the FGD system during the baseline and organic acid addition tests, and operation results present a qualitative discussion of how the operation of the FGD system was affected by the organic acid tests. The discussion of additive effects summarizes observations specific to the three additives tested during the program.

5.1 PERFORMANCE RESULTS

The San Miguel test program examined different organic acids over a range of operating conditions. To quantify how changes in organic acid composition or concentration affect the costs of operating the FGD system, several key measures of process performance must be compared.

Table 5-1 summarizes these data for each of the organic acid addition tests. These data represent averages of the major factors which affect the costs of organic acid use at San Miguel. The majority of the data are for tests using the DBA mixture supplied by DuPont. Those tests cover a range of operating conditions including varying concentrations of DBA and tests with and without manganese in the FGD system. The range of the data made it possible to interpolate test results and thereby optimize the savings associated with DuPont DBA addition. The data for the organic acid additives supplied by Badische Corporation (EP-306 and EP-501) are at one condition for each additive. Therefore, it was not possible to estimate the optimum

TABLE 5-1. SAN MIGUEL TEST SUMMARY

ITEM	TEST ID							
	DuPont 1	DuPont 2	DuPont 3	Badische 1	Badische 2	Mn 1	Mn 2	Mn 3
BUFFER CAPACITY (ppm)	632	1415	2018	461	125	643	574	629
BUFFER TYPE	DuPont DBA	DuPont DBA	DuPont DBA	EP-306	EP-501	DuPont DBA	DuPont DBA	DuPont DBA
MANGANESE CONC. (ppm)	1	1	1	1	1	6.9	10.8	10.8
ORGANIC ACID CONSUMPTION								
a. lb/hr	293	535	582	196	241	326	271	321
b. lb/ton SO2	18.0	34.4	35.2	12.9	17.1	28.7	24.4	29.7
INLET SO2 (lb/MMBtus)								
a. Coal Analysis	7.41	7.41	7.41	7.07	7.07	5.19	5.19	5.19
b. SO2 Monitors	7.68	6.45	7.55	7.20	6.48	6.08	5.70	5.59
SO2 EMISSIONS (lb/MMBtu)	1.02	0.98	0.77	1.00	1.07	1.07	1.02	1.10
SO2 REMOVAL - MODULES (%)								
a. Coal Analysis	91.1	94.1	95.8	87.5	87.8	84.0	86.0	83.6
b. SO2 Monitors	90.8	94.1	96.1	82.4	86.5	90.3	91.4	94.1
SO2 REMOVAL - SYSTEM (%)								
a. Coal Analysis	86.2	86.8	89.7	85.9	84.9	79.4	80.4	78.8
b. SO2 Monitors	86.7	84.8	89.9	86.1	83.5	82.4	82.1	80.3
SO2 REMOVED (tons/hr)	16.3	15.6	16.6	15.2	14.1	11.5	11.2	11.0
LIMESTONE UTILIZATION (%)								
a. Absorbers	85.9	86.3	74.0	65.7	79.1	79.3	82.1	82.3
b. Quenchers	85.0	89.4	91.3	82.7	84.8	87.8	92.6	88.4
OPERATING pHs								
a. Absorbers	5.83	5.77	5.82	5.79	6.05	5.90	5.90	5.86
b. Quenchers	5.48	5.47	5.47	5.69	5.86	5.56	5.57	5.64
GAS FLOWS (wet Mscfm)*								
a. Modules	1296	1266	1268	1358	1301	1295	1295	1300
b. Bypass	73.5	106.9	86.7	26.5	29.5	75.3	91.4	78.4
c. Reheat	109.9	57.1	192.0	182.7	192.5	143.0	131.7	167.1
MAXIMUM BYPASS (wet Mscfm)*								
a. Coal Analysis	89.4	130.5	150.5	48.5	50.9	84.6	115.8	78.9
b. SO2 Monitors	77.3	162.7	150.4	-39.0	53.5	127.4	162.2	201.9
SULFITE OXIDATION (%)								
a. Absorbers	24.9	25.6	26.1	24.2	26.3	26.9	29.0	35.9
b. Quenchers	24.9	25.3	22.0	25.2	25.2	24.3	27.2	33.1

* Mscfm = 1000 standard (60°F, 29.92 inHg) cubic feet per minute.

concentrations of these additives; and in the case of the EP-306 additive, it was not technically feasible to operate at higher buffer capacities.

In order to evaluate the test results summarized in Table 5-1, several comparisons should be made. Also, to complete the economic analysis of the DuPont DBA additive, correlations which relate buffer capacity to organic acid consumption, flue gas bypass, and limestone utilization are required. The following discussion is an examination of the data summarized in Table 5-1. It covers the three major factors which affect the costs of organic acid addition to San Miguel's FGD system:

- Organic acid consumption,
- Limestone utilization, and
- Flue gas bypass

The discussion of each of these cost factors includes an explanation of how the results were calculated and presents correlations developed for use in the economic analysis presented in Section 6.

5.1.1 Organic Acid Consumption

Organic acid consumption is one of three significant factors which affect the costs of acid addition to the San Miguel FGD system. Previous tests have shown that organic acid consumption in an FGD system can be a function of several factors including buffer capacity (which for a given acid or acid mixture is proportional to concentration), sulfite oxidation, acid composition, manganese concentration, pH, etc. If any of these factors can be controlled, it is important to quantity how they effect organic acid consumption and also how they effect limestone utilization and bypass rate.

Figure 5-1 presents the organic acid consumption rates for the San Miguel tests as a function of buffer capacity (not concentration). The figure also includes a curve which is a regression fit of the DuPont DBA test results. It should be noted that the consumption rates in Figure 5-1

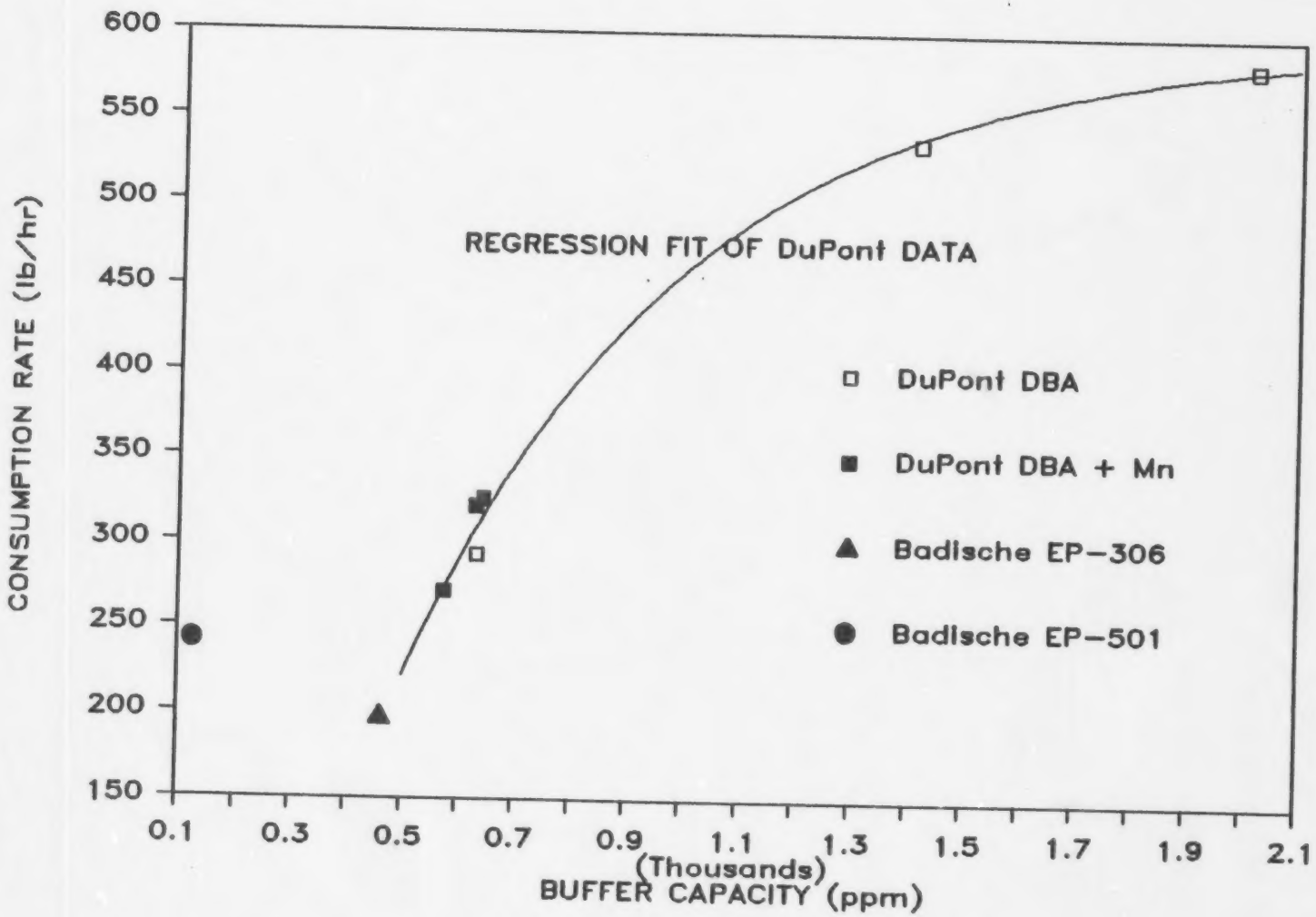

Figure 5-1. Organic Acid Consumption vs Buffer Capacity for all Organic Acids Tested.

represent the total organic acid loss rate in the San Miguel system. As such, the consumption rates include:

- Losses due to chemical degradation of the organic acids,
- Losses due to precipitation or co-precipitation of the organic acids with the calcium-sulfur salts produced in the system,
- Losses due to organic acids present in process liquor entrained with the waste solids.

No attempt is made to separate the fraction of acid lost by each mechanism in this report.

The consumption rates presented in Figure 5-1 are based on system material balances which account for: (1) the organic acids added to the system during a test, and (2) the accumulation of organic acids in the system over the duration of a test. The acid addition rates were determined by hourly measurements of acid flow and analyses of the concentrated acids. Accumulation rates were determined by measuring the buffer capacity in all tanks in the FGD system at the start and end of each test. The buffer capacity shown in Figure 5-1 is a time weighted average of all the absorber and quencher modules which operated during a test. Samples of each operating absorber and quencher were taken daily during each test.

Figure 5-1 illustrates several interesting results. First, it indicates that the DuPont DBA consumption rate increases at a less than linear rate over the range of buffer concentrations tested. In other words, a doubling of the DBA buffer capacity does not double the DBA consumption rate. This result is consistent with laboratory results for adipic acid which showed that consumption is proportional to acid concentration to the 0.55 power[1] (the exponent for the curve in Figure 5-1 is approximately 0.6). Since the rate of organic acid degradation decreases at increasing buffer capacities, there is a less than proportional cost associated with

higher buffer capacities. Under some circumstances, this could make operating at higher buffer capacities more cost effective (cost trade-offs are covered in Section 6).

Another important result illustrated in Figure 5-1 is the effect of manganese on the DBA consumption rates. As shown, the DuPont tests with manganese do not differ appreciably from the comparable DuPont test without manganese. This is in contrast to results reported by other investigators. Previous studies have shown that manganese can reduce the chemical degradation part of adipic acid losses to near zero[1].

The reasons for the differences between the San Miguel manganese tests and previous tests are not clear. It may be that differences between pure adipic acid and the DBA acid mixture tested at San Miguel can account for the fact that manganese does not appear to have a significant effect on consumption. Another possibility is that the operating conditions during the manganese tests at San Miguel were outside the range in which manganese affects the organic acid degradation mechanism. Also, it may be that chemical degradation represents only a small faction of the overall organic acid consumption rate at San Miguel. In any event, no benefit from manganese addition was observed.

A third important result illustrated by Figure 5-1 is the relative consumption rates of the three organic acid additives tested at San Miguel. As shown, the two organic acid mixtures supplied by Badishe have significantly different consumption rates relative to each other. The additive EP-306, which is a mixture consisting primarily of mono-basic hydroxycaproic acid and dibasic adipic acid, shows a consumption rate which appears to be in line with the consumption rates for the DuPont DBA mixture. However, EP-501 additive, which is a mixture consisting primarily of dibasic maleic acid, has a high consumption rate relative to the buffer capacity provided. Figure 5-1 shows that although the buffer capacity for the maleic acid test is about one-fifth of that in the lowest buffer capacity DuPont additive test, the consumption rate of EP-501 is about 80 percent of the DuPont test.

This indicates that EP-501 has a very high consumption rate relative to the buffer capacity provided when compared to the DuPont DBA. Also, the consumption rate for the maleic acid test is actually higher than that for the EP-306 additive test while the buffer capacity is less than one-third of that provided by EP-306.

The reason why the EP-501 additive appears to have a relatively high consumption rate is not clear. One factor which may contribute is the fact that although the buffer capacity provided by EP-501 is relatively low, the concentration of acids in solution may actually be much higher. This is because EP-501 consists primarily of maleic acid which does not buffer as well as other dibasic acids in the pH range 3 to 6 (see Section 4.2). Since the rate of acid loss is probably a function of concentration and not buffer capacity, maleic acid would be expected to show higher consumption rates when compared with other dibasic acids on the basis of buffer capacity. However, buffer capacity is a fair basis for comparing different organic acids because it is buffer capacity (not concentration) which benefits the operation of the FGD system.

One final item regarding the organic acid consumption rates at San Miguel is the effect of inlet SO_2 concentration on consumption rates. Previous work has often normalized organic acid consumption rates based on the quantity of SO_2 removed in an FGD system[1,3]. This stems from early work which anticipated that the primary source of organic acid losses in the system would be in the process liquor which is entrained with waste solids. Since the waste solids production rate is directly related to SO_2 absorption, it was assumed that the organic acid loss rate would also be a function of SO_2 absorption. However, in the initial tests with DBA, the actual acid consumption rates were found to be 13 to 14 times the rates predicted based on acid losses via entrained process liquor[3]. This indicated that "other" mechanisms tend to dominate the rate at which acids are lost from the system. However, it was still assumed that these other mechanisms for acid loss were related to the quantity of SO_2 absorbed in the FGD system.

Figure 5-2 presents data from San Miguel which indicates that the primary mechanism of organic acid loss may not be related to SO_2 absorption. This figure shows that, at equivalent buffer capacity, the SO_2 absorption rate does not appear to affect the organic acid consumption rate. The variation in SO_2 absorption rates is a result of variations in coal sulfur content (from 1.4 to 2.0). It should be noted in reviewing these results that the test with a high SO_2 absorption rate was conducted without manganese in the FGD system while all the tests at low SO_2 absorption rates were coincidentally conducted with manganese. As a consequence, variables are confounded between the two groups of tests and should therefore be viewed with caution.

5.1.2 Limestone Utilization

Limestone utilization is another factor which has a significant impact on the costs associated with organic acid addition. The major driving force for use of an organic acid additive at San Miguel was the potential for reducing limestone consumption by an amount which would more than off-set the cost of the organic acid additive and the capital charges for an organic acid feed system. Some additional benefits from reduced limestone consumption were also expected (See Section 5.2), but were not considered in the initial evaluation of the costs of organic acid addition.

Table 5-2 summarizes the limestone utilization data collected during the test program at San Miguel. It includes data from baseline conditions (prior to organic acid addition) and each of the organic acid tests. Data are presented for both the quench and absorber loops although the measurement of the quench solids represents overall limestone utilization since it is these solids which are ultimately discharged from the FGD system. As shown, the baseline utilization measured at San Miguel averaged 70 percent while the organic acid addition tests had measured utilizations ranging from 83 percent to nearly 93 percent. The measured utilizations for the organic acid addition tests are based on samples collected from operating quench

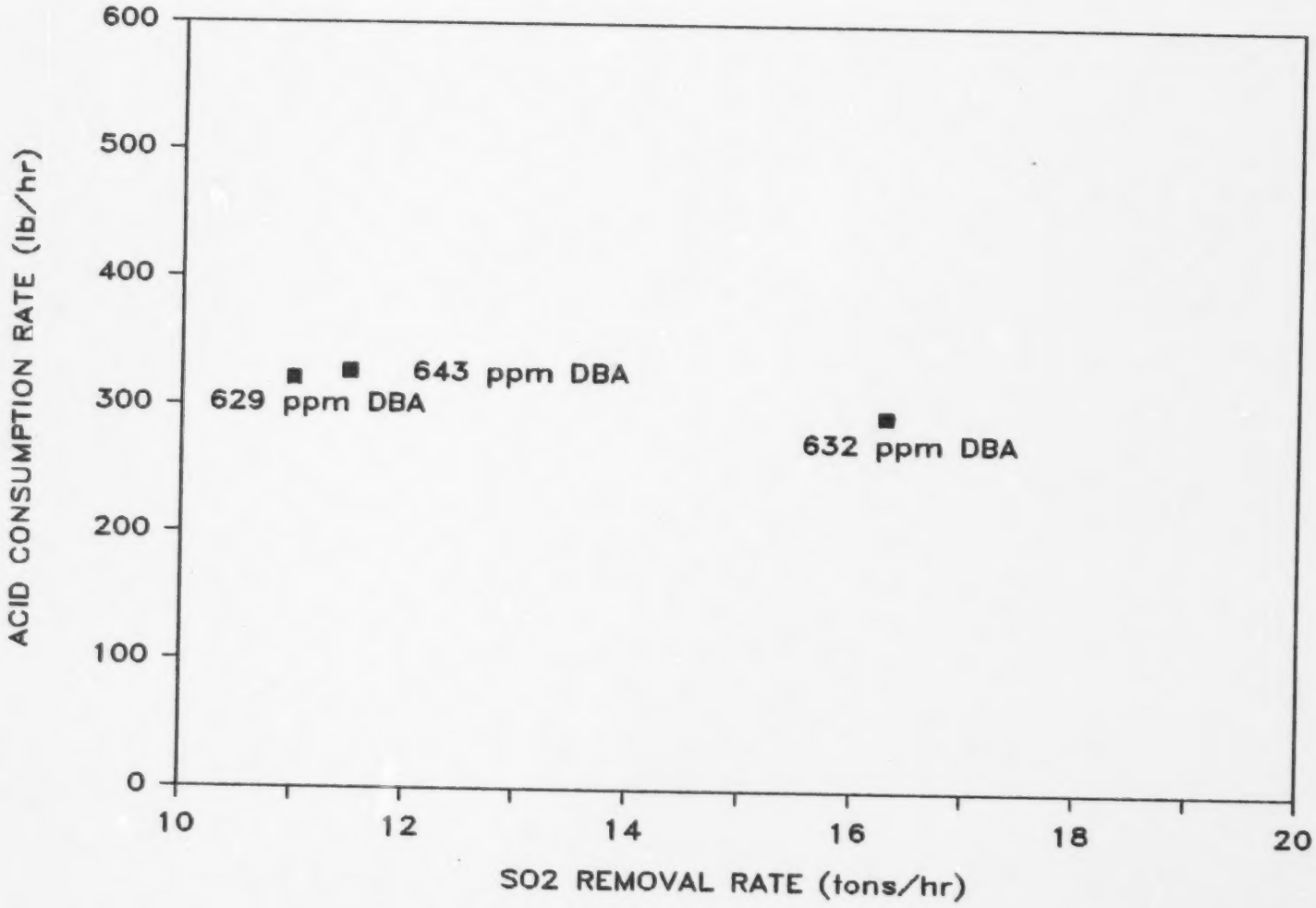

Figure 5-2. DBA Consumption as a Function of SO_2 Removal Rate for DuPont DBA.

TABLE 5-2. SAN MIGUEL TEST AVERAGES - OXIDATION, UTILIZATION, AND PH

Test ID	Adsorber			Quencher		
	Oxidation	Utilization	pH	Oxidation	Utilization	pH
Baseline	20.0%	66.9%	6.16	18.9%	70.0%	6.09
DuPont 1	24.9%	85.9%	5.93	24.9%	85.0%	5.53
DuPont 2	25.6%	86.3%	5.87	25.3%	89.4%	5.49
DuPont 3	26.1%	74.0%	6.04	22.0%	91.3%	5.58
Badische	24.2%	65.7%	6.05	25.2%	82.7%	5.79
Maleic	26.3%	79.1%	6.16	25.2%	84.8%	5.84
Manganese 1	26.9%	79.3%	5.87	24.3%	87.8%	5.67
Manganese 2	29.0%	82.1%	5.85	27.2%	92.6%	5.64
Manganese 3	55.9%	82.3%	5.89	33.1%	88.4%	5.65

loops each day during the tests. These samples were then analyzed to determined the calcium carbonate content of the solids and, based on measurements of solids oxidations and inerts at the end of each test, the limestone utilizations were estimated.

Since the utilizations shown in Table 5-2 are based on a limited number of samples, it is possible that an upset in process operation at or around the time one set of samples were collected could skew the utilization results for a given test. In order to obtain a more balanced measure of utilization, continous process pH measurements made during the tests can be used as an average indication of utilization. To do this, a correlation of pH vs measured utilization is needed.

Figure 5-3 presents a correlation of pH vs utilization for all the utilization measurements made during the San Miguel test program. As the figure shows, utilization is relatively insensitive to pH below a pH of 5.6 to 5.7 and it drops off rapidly as pH rises above 5.9. The figure also shows quite a bit of data scatter. This is attributed to several factors including variations in the limestone grind and possible effects of organic acid concentration on limestone utilization.

The correlation presented in Figure 5-3 can be used for several purposes. It serves as a basis for calculating limestone utilization in the economic analysis. It can also be used as an operating guideline for San Miguel in selecting pH set points for quencher loop operation. As shown, operation at pH 5.4 or less will on the average result in a limestone utilization of 95 percent and there will be very few excursions below 90 percent utilization.

As mentioned above, some of the data scatter in Figure 5-3 may be a result of differences in organic acid concentration. Some investigators have indicated tht organic acid buffers can promote limestone dissolution by buffering the pH at the surface of limestone particles in much the same way they act to enhance SO_2 removal in an absorber[2]. However, measurements

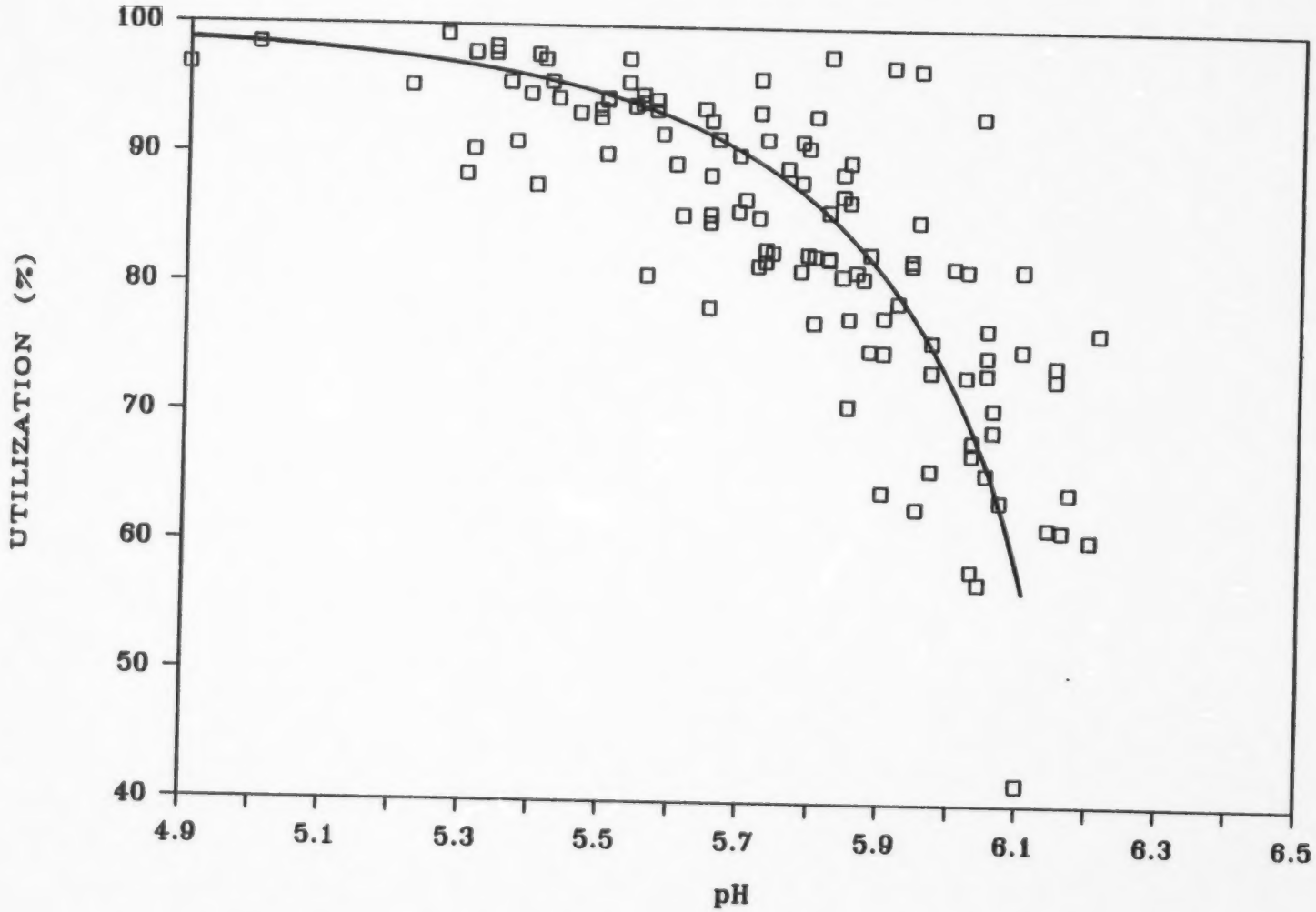

Figure 5-3. Limestone Utilization as a Function of Slurry pH in the San Miguel FGD System.

during the Springfield organic acid addition tests were unable to document an improvement in utilization due to the use of organic acids [3]. This is also the case with the San Miguel data. Figure 5-4 presents the ratio of measured-to-predicted limestone utilization as a function of buffer capacity. The measured utilization used to calculate the ratio represents average utilizations in the quench or absorber module from each of the organic acid addition tests. The predicted utilization represents the average utilizations predicted from the correlation shown in Figure 5-3 and the pHs of absorber or quench samples from each organic acid addition test. Use of the measured/predicted ratio normalizes the utilization data for the effect of pH and thus should allow any utilization vs buffer capacity trends to be observed. As shown in Figure 5-4, there is no significant relationship between buffer capacity and limestone utilization. If organic acids did improve limestone utilization, the measured-to-predicted utilization ratio should increase with increasing organic acid buffer capacity.

5.1.3 SO_2 Removal Efficiency/Flue Gas Bypass

The third major factor which affects the economics of organic acid addition at San Miguel is the amount of flue gas which can be bypassed around the absorber. Flue gas bypass lowers the requirement for reheat steam and therefore improves boiler efficiency. This provides a cost savings to San Miguel. The amount of flue gas which can be bypassed is determined by several factors at San Miguel including the SO_2 removal efficiency across the scrubber modules and the inlet SO_2 levels.

During the organic acid addition tests, three levels of DuPont DBA additive were tested and 3 levels of module SO_2 removal were determined. As a result, it is possible to correlate both SO_2 removal and bypass rates to buffer capacity in the San Miguel system. By developing such a correlation, it then became possible to evaluate the cost trade-off between organic acid consumption rates and bypass rates at varying levels of buffer capacity.

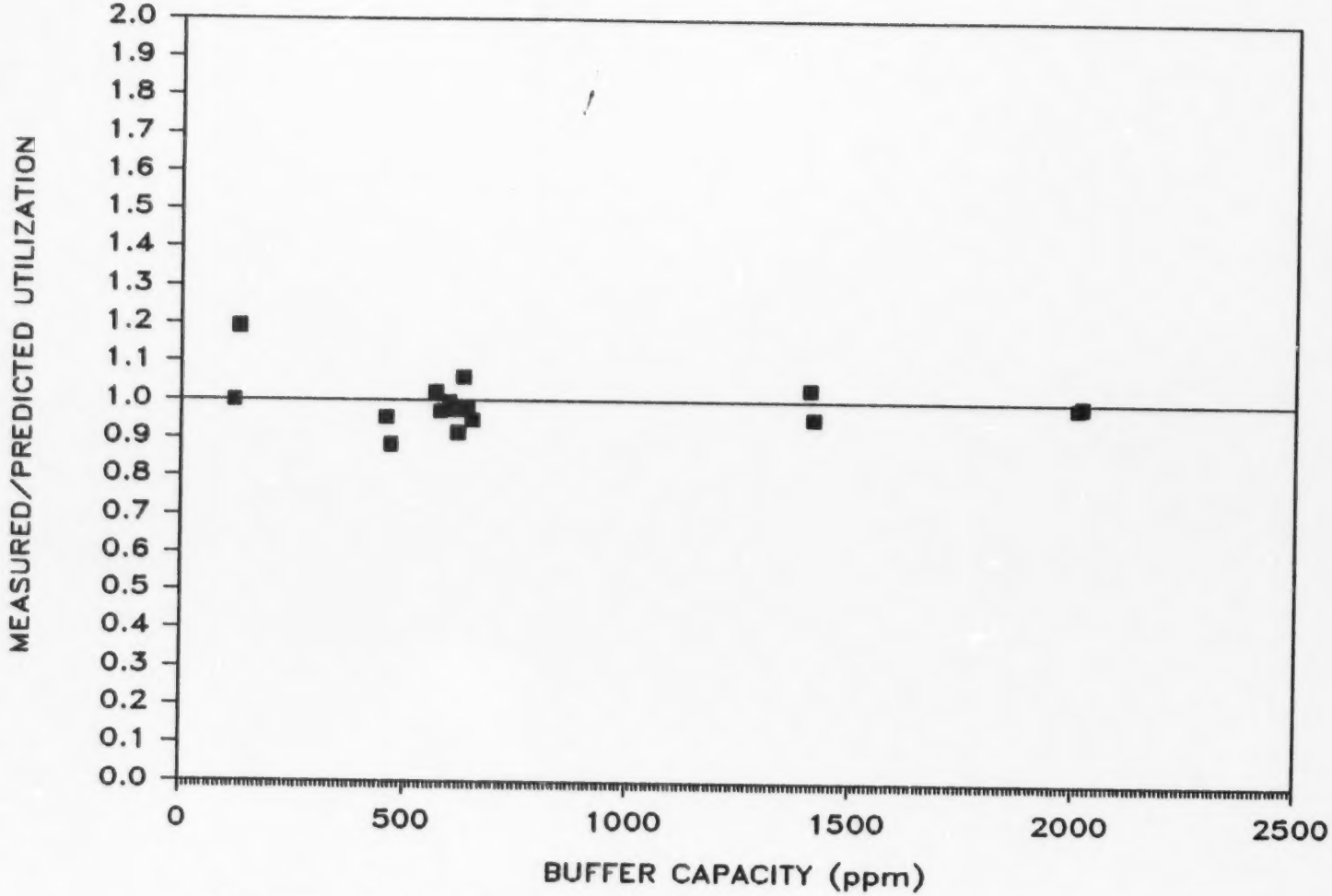

Figure 5-4. Ratio of Measured Limestone Utilization to Predicted Utilization as a Function of Buffer Capacity.

Figure 5-5 presents the estimated maximum bypass rates as a function of buffer capacity for the DuPont DBA tests conducted during December 1983. Results for the other organic acid tests and for the DuPont tests with manganese are not included, primarily because of differences in coal sulfur levels during these tests. The maximum bypass rates presented in Figure 5-5 are calculated from actual bypass rates, SO_2 removals across the quench and absorer modules, and the flue gas flowrate through the modules. The maximum bypass rates differ from actual bypass rates because they are normalized to an SO_2 emission rate of 1.1 $lb/10^6$ Btu. This was necessary since the emission rates during the DuPont DBA tests varied from 0.77 to 1.02 lb $SO_2/10^6$ Btu. It was necessary to adjust the bypass rate to a constant SO_2 emission level to calculate the potential cost benefits available at higher buffer capacities. An emission rate of 1.1 $lb/10^6$ Btu was selected because it represents about a 10 percent safety factor below the current 1.2 $lb/10^6$ Btu emisison limit and it should be possible to attain operation at 1.1 $lb/10^6$ Btu with reasonable care.

Figure 5-5 shows that the maximum bypass increases as the organic acid buffer capacity increases. This is a result of improved SO_2 removal which occurs at higher buffer capacities. The figure also shows that the amount of bypass possible approaches a limit at higher buffer capacities. This indicates that the cost benefits associated with flue gas bypass are limited.

Obviously, there is a trade-off between increased bypass rates and increased organic acid consumption which occurs at higher buffer capacities. The relationships presented in Figure 5-5 and 5-1 are used along with specific cost data in Section 6 to determine the economic optimum DBA level for the San Miguel FGD system. Table 5-1 summarizes these data for the baseline tests and each of the organic acid addition tests.

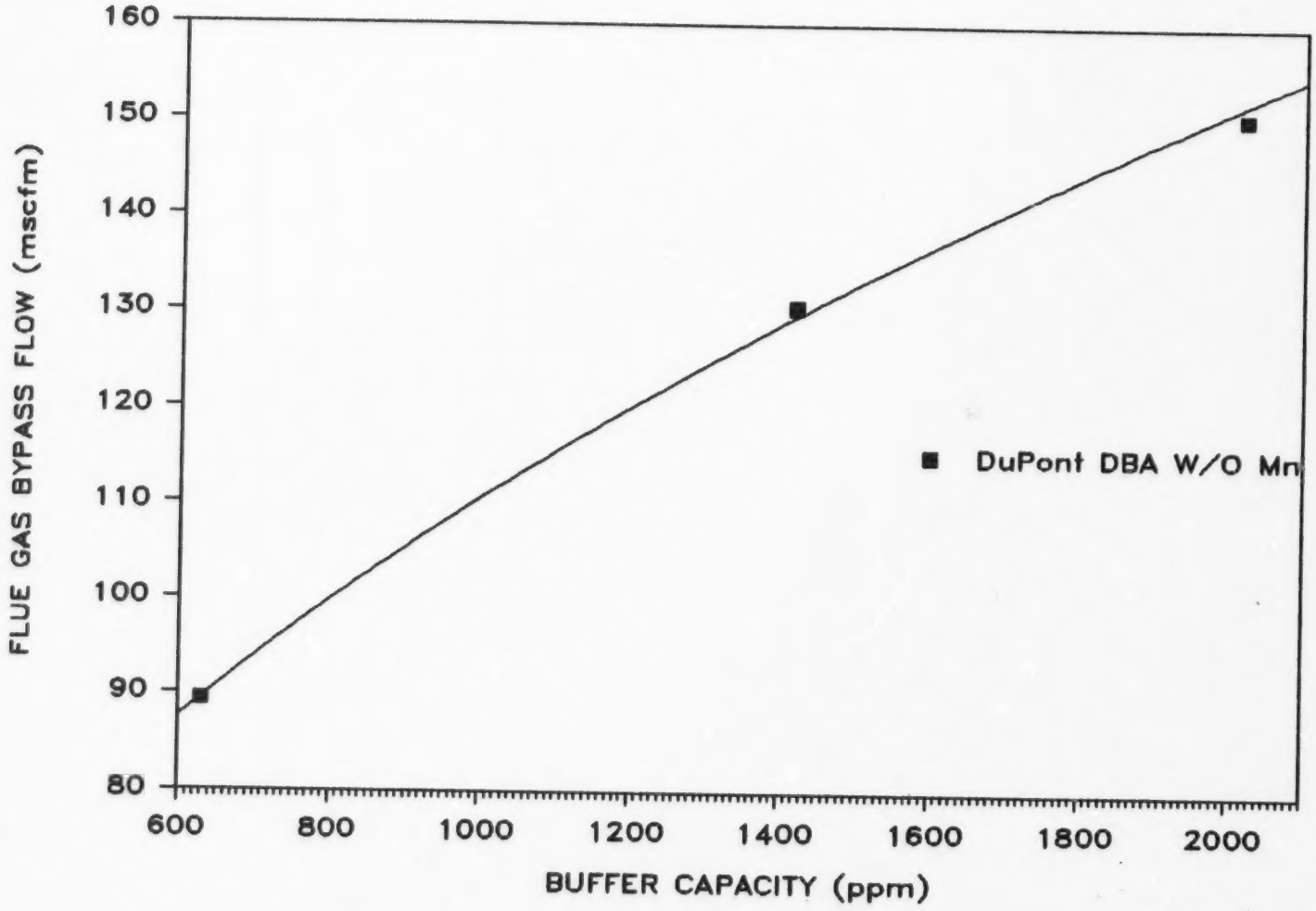

Figure 5-5. Flue Gas Bypass Flow vs Buffer Capacity for the DuPont DBA Tests.

5.2 OPERATION RESULTS

In addition to the quantitative results of the San Miguel organic acid tests, there were some qualitative observations made during the test program which may be of interest to utilities considering an organic acid additive to enhance the performance of a limestone FGD system. The discussion which follows summarizes those observations. Areas which are addressed include:

- pH meter maintenance and operation,
- thickener operation,
- absorber and mist eliminator pluggage,
- foaming in the recirculation tanks,
- FGD system water balance, and
- corrosion of the DBA feed system.

A general discussion of each of these areas is provided along with comments relating to specific test conditions where appropriate.

pH Meter Maintenance and Operation

Prior to the use of organic acid addition at San Miguel, pH was not a critical operating variable in the FGD system. Limestone addition was controlled by the pH feedback loop, but this was often overridden by the need to meet the 1.2 $lb/10^6$ Btu SO_2 emission standard. In such cases, limestone was added to the FGD system regardless of the pH. After the start of the organic acid addition tests, accurate pH readings became more important. It was necessary to control the quench loop pH at 5.4 to obtain the maximum cost benefit from the use of organic acid in the FGD system. Only by operating at this lower pH was it possible to reduce limestone stoichiometry and therefore reduce operating costs. Also, operation at lower pH's in the absorber contributed to the reduced tendency for the absorber trays and mist eliminators to plug.

San Miguel has a regular pH meter maintenance program which includes calibration of the pH monitors once a shift and a check to insure that there is adequate sample flow past the pH electrodes. Typical problems include pH meter drift, sample line pluggage, and breakage of pH electrodes. Of these problems, the last two are more serious. Plugged sample lines cause the pH meter to read high while broken electrodes can cause erratic readings. Before the use of organic acid at San Miguel, the existing pH meter maintenance schedule was probably more than needed. However, after the start of the organic acid tests, the pH meter maintenance schedule was just enough to maintain good pH control; and an increase in the frequency of pH meter maintenance to twice a shift would have been useful. Most of the time, system pH measurements were accurate, but there were a number of occasions when pHs were higher than the set point required. During these periods, limestone use was excessive. No cost analysis of these pH excursions was completed, but there is a definite cost penalty associated with pH drift.

In summary, San Miguel's excellent pH monitor maintenance schedule did not require any changes once organic acids were added to the FGD system. However, in many plants were the pH meters receive less attention, an improved maintenance schedule will be needed to accrue the full cost savings associated with organic acid addition; and in some cases, an improved pH monitoring system may even be needed.

Thickener Operation

One noticable change in FGD system operation occurred once organic acids were added to the thickeners. Prior to the start of organic acid addition, the thickeners were often "cloudy" and they operated with only one clear sample port*. In addition, a flocculent was used to aid in setting of

*Sample taps are located in the side of each thickener at regular intervals. The number of "clear ports" is the number of taps from the top of the thickener which discharge clear liquor when sampled.

fine particles which were responsible for the "cloudy" appearance. Shortly after the start of organic acid addition to the system, thickener operation improved dramatically. Three clear ports in the thickener became common and the of floccuent addition rate was reduced.

It is believed that the improvement in thickener operation is an indirect result of organic acid addition to the FGD system. The direct cause is the reduction in operating pHs which corresponds to a reduction in the amount of excess limestone in the system. At lower excess limestone levels in the FGD system, there is a reduced load on the thickener (i.e., less solids are disposed of) which would tend to improve operation. In addition, lowering the excess limestone would be expected to significantly reduce the number of very fine particles in the system. This should also help thickener operation.

It is likely that the change in excess limestone is the major factor which contributed to improved thickener operation. Other contributing factors include:

- Increased sulfite oxidation was also observed at the lower operating pHs associated with organic acid addition. Calcium sulfate solids formed as a result of increased oxidation would be expected to settle better than calcium sulfite solids.

- It is also possible that operation at lower pHs caused a change in the size and/or shape of calcium sulfite solids which promotes settling.

It is believed that one or more of these factors contributed to the improvement in thickener operation at San Miguel. However, the individual contribution of these factors was not documented and therefore cannot be quantified.

The improvement in thickener operation discussed above was observed during all but one of the organic acid addition tests. The one exception occurred during the tests with the Badische additive, EP-306. During these tests, foam from the quench tank was carried to the center well of the thickeners. The foaming action tended to cause the center well to overflow into the thickener and as a consequence, the cloudiness in the thickeners returned. This problem was one reason why the planned tests with EP-306 were cancelled.

Absorber and Mist Eliminator Pluggage

A number of changes in FGD system operation were made possible once organic acid addition was initiated at San Miguel. As a result of those changes, several improvements in operation were osbserved. One of the most significant improvements was virtual elimination of scaling and plugging of the absorber trays and mist eliminators. This resulted in a significant reduction in the maintenance effort required to keep the FGD system running.

Prior to organic acid use, San Miguel routinely had a full time (40 hrs/week), 5 to 10 person crew cleaning absorber trays and mist eliminator passages in the spare module. However, after the start of the organic acid tests, module inspections revealed little or no scale in the absorbers or mist eliminator and the cleaning effort was substantially reduced. The biggest problem which remained was pluggage of spray nozzles in the absorbers with deposits which formed and sloughed off the absorber and quencher walls.

The reduction of absorber tray and mist eliminator plugging at San Miguel is attributed to the changes which were made possible by organic acid addition. Two of the most significant changes were:

- Operation at an absorber pH of 5.8 - at this pH there is less excess limestone in the recirculating slurry than during previous operation at pH 6.3 to 6.5. Studies have shown that at high

levels of excess limestone in the absorber, limestone dissolution can result in localized areas of high relative saturation with respect to calcium sulfite and sulfate. This can cause scaling, especially on mist eliminator surfaces[4].

- Operation at lower absorber gas velocities - before organic acid addition, removal efficiency in the FGD system was just at the level required by regulations and little flue gas bypass of the quench-absorber modules was possible. However, with organic acids, it became possible to bypass up to 10 percent of the flue gas around the scrubber modules. This lowered the gas velocity through the modules and would be expected to reduce carryover to the mist eliminators thereby reducing the tendency for the mist eliminators to plug with solids.

The net effect of these and other operating changes was a significant reduction in FGD system maintenance requirements.

Foaming in the Recirculation Tanks

One problem which has been observed with the use of some organic acid mixtures in an FGD system is foaming. Foaming is caused by soap-like impurities in organic acid mixtures and it can be a significant operating problem. During the tests at San Miguel, foaming was obseved under all conditions, but the severity of the foaming problem varied. During the tests with the DuPont supplied DBA, foaming was first observed at a buffer capacity of about 600 ppm. At this level of buffer capacity, the recirculating tank levels were reduced from 19 to 17 feet to provide 5 feet of freeboard in the tank and thereby prevent the tanks from foaming over. At higher levels of DuPont DBA, the foaming became more severe and at a buffer capacity of 2,000 ppm, the recirculation tanks periodically overflowed. However, no other adverse effects of foaming were observed during this test.

Following the DuPont DBA tests, the FGD system was purged of organic acid by discontinuing addition of the DBA. Tests were then initiated using the organic acid mixture supplied by Badische Corporation (EP-306). During the first of 3 scheduled tests using this material, the foaming in the recirculation tanks was more severe at a buffer capacity of around 500 ppm than during the DuPont DBA tests at a 2,000 ppm buffer capacity. In response to this problem, San Miguel lowered the recirculation tank levels an additional 2 feet (to 15 feet) which provided a total of 7 feet of freeboard. Even at this tank level, the Badische material caused the tanks to foam over almost continuously. In addition, other problems which San Miguel attributed to the severe foaming developed as the test continued. These problems included:

- Foam in the Thickener - This caused solids to overflow from the center well which resulted in solids being carried into the thickener overflow tank. Also, the weight percent solids in the thickener underflow was reduced.

- Plugging of pH Sample Lines - Operators indicated that pH probes were plugging much more frequently during the Badische test, but there is no obvious reason why foaming would cause this. Problems with the pH probes also caused pH to drift from the set points and resulted in poor reagent utilization.

Because of the problems experienced with foaming of the Badische EP-306 additive, planned tests at higher buffer capacities were cancelled. In place of these tests, San Miguel agreed to test another Badische additive (EP-501) which consisted primarily of maleic acid. During the test with EP-501, no significant foaming problems were observed.

FGD System Water Balance

One minor change which occured with organic acid addition was a reduction in the quantity of water consumed by the FGD system. At the lower

limestone stoichiometries made possible with the use or organic acids, the quantity of waste generated by the FGD system was reduced by approximately 17 percent by weight. Assuming that the weight fraction of water in the solids from the vacuum filter are relatively constant, a decrease in the total mass of solids results in a slight decrease in the total water consumed by the FGD system (i.e., evaporated water plus water associated with the waste solids). For San Miguel this change was estimated to be about 5 percent of the FGD system's total water requirement and it did not have a significant impact on the system water balance. For other systems, especially those with a positive FGD system water balance, this could prove to be more significant.

Corrosion of the Organic Feed System

San Miguel had a serious problem with corrosion of the organic acid feed system during the initial months of operation. Corrosion occurred in all areas of the feed system including the tank heater (which failed after only 20 days of operation), lines, valves, and the tank itself. This problem has proved quite costly, increasing San Miguel's capital investment for the organic acid system by nearly 50 percent. Corrosion also caused several interruptions in organic acid feed which resulted in a return to high pH operation in the FGD system.

As mentioned earlier, all the original materials of construction in the San Miguel organic acid feed system were 304 SS. This is the material used by DuPont for handling and storing DBA and they have reported no problems. In addition, other plants have used 304 SS successfully for handling DBA.

It appears, then, that the problems at San Miguel are site-specific. It is believed that San Miguel's corrosion problems are a result of mixing FGD process liquor and cooling tower blowdown (CTB) water with organic acids in the storage tank. Initially, CTB water was added to the organic acid mixture to reduce the acid concentration and thereby reduce the temperature at which the organic acids would precipitate from solution. Later, during

cold weather, FGD process water was added to the feed tank because it was at a higher temperature than the CTB water.

An analysis of pipe samples from San Miguel's organic acid feed system have shown severe pit corrosion of the material. This corrosion was attributed to chloride attack of the metal under the highly acidic conditions (pH = 3.0) present in the DBA feed system. No chloride measurements were made of the DBA material itself, but an analysis of the FGD process liquor and CTB water showed chloride concentrations ranging from 5000 to 9000 ppm.

Since the feed system corrosion became severe, San Miguel has replaced the stainless steel feed lines with PVC and has repaired the feed tank twice. They have also avoided adding water to the organic acid feed. This has minimized the current problem, but the initial corrosion problem obviously caused an additional capital expense. Utilities considering the use of organic acids should benefit from the negative experience at San Miguel. The solution is to either avoid addition of chloride containing water to the organic acid feed or use a chloride resistent material such as fiberglass or PVC.

Summary

Operating experience at San Miguel has shown some benefits from organic acid addition which could not be quantitifed. These operating benefits include:

- improved thickener operation, and
- reduced absorber and mist eliminator plugging and scaling.

These benefits may not be a direct result of the presence of organic acids in the system. Rather they are a result of the changes in FGD system operation made possible by the use of organic acids.

Some other aspects of organic acid addition at San Miguel include:

- Requirement for more accurate pH measurement and control--At San Miguel this was not a problem, but it may be for other utilities.

- Foaming in the recirculation tanks--This problem varied depending on the organic acid source and concentration. With the Badische additive EP-306, foaming was so severe the system could not be operated normally at low (about 500 ppm) buffer capacities.

- Decrease in FGD system water consumption--At San Miguel this was not a problem, but it could be for a utility which already has a positive FGD system water balance by making the water balance even more positive.

- Corrosion of the organic acid feed system--This has proven costly to San Miguel. It can and should be avoided in future installations.

5.3 ADDITIVE EFFECTS

Of the three organic acid additives tested, only the DuPont DBA was examined over a range of conditions. The Badische supplied acids EP-306 and EP-501 were tested at only one level. The results of these tests permit two general comparisons. The DuPont material provided good performance over the range of conditions tested. However, foaming did begin to be a problem at a buffer capacity of 2,000 ppm. The Badische material EP-306 was only tested at a buffer capacity of about 500 ppm, but at this level, foaming was more severe than that observed for the DuPont material at 2,000 ppm. Because of the severe foaming, planned tests using EP-306 at higher buffer capacities were cancelled. The test with the Badische additive EP-501 did not exhibit any unusual foaming problems.

In terms of acid consumption rates, the DuPont material exhibited a less than linear increase in consumption as a function of buffer capacity. The Badische additive EP-306 appeared to have a consumption rate similar to the DuPont material. The additive EP-501 had a consumption rate which appeared to be significantly higher than either the DuPont material or the EP-306 additive. Comparisons of the consumption rates of these additives should be made with caution, however, because it was not possible to test the Badische additives in the same range of buffer capacities examined for the DuPont additives.

5.4 REFERENCES

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SECTION 6
ECONOMIC ANALYSIS

The overall objective of the San Miguel test program was to expand the technical and economic data base on organic acid addition to commercial FGD systems. This section presents the results of a site-specific economic analysis based on the results of the test program (see Section 5 for details). Items included in the economic analysis are:

- Optimum costs for the DuPont additive,
- First year costs for the three additives tested, and
- A 15-year cumulative net present worth analysis for the three additives tested.

Each of these items are discussed below.

6.1 OPTIMUM COSTS FOR THE DUPONT DBA ADDITIVE

Tests with the DuPont DBA additive covered a range of buffer capacities and included operation with and without manganese in the FGD system. With the data collected during these tests, it was possible to determine an optimum buffer capacity (based on costs) for the DuPont DBA. The optimum was determined by calculating the 15-year cumulative net present worth (CNPW) associated with additive addition for buffer capacities varied over the range 600 to 2,000 ppm (which corresponds to the range of buffer capacities examined during the test program). Details of how the CNPW was evaluated including the economic bases, escalation factors, and plant design factors, are presented in Section 6.3.

Figure 6.1 presents the results of the CNPW analysis for varying concentrations of the DuPont DBA additive. Costs for manganese addition are not included since the test results showed no benefit from manganese. As shown, cost savings are a maximum at the lowest buffer capacity tested and they decline rapidly as buffer capacity increases from 600 to 1,400 ppm. Above a buffer capacity of 1,400 ppm, costs continue to decine, but at a gradual rate. These results indicate several things concerning the cost benefits of DBA addition. The first is that most of San Miguel's economic benefit from DBA addition occurs at relatively low buffer capacities. Cost savings which result at higher buffer capacities (e.g., increased flue gas bypass credits) do not offset the costs of a concurrent increase in additive consumption.

The results presented in Figure 6-1 seem to imply that additional cost savings may result at even lower buffer capacities. However, caution should be exercized in extrapolating the San Miguel test results. Operating experiences during the test program indicated that at buffer capacities much lower than 600 ppm, it became difficult to meet the 1.2 $lb/10^6$ Btu SO_2 emission limit and operate the absorber and quench loops at low pH's. During the tests with the Badische addivites at buffer capacities less than 500 ppm, high pH's were required to maintain SO_2 emissions within limits. This resulted in a return of the absorber and mist eliminator plugging problems which were prevalent before the organic acid addition test program started.

6.2 FIRST YEAR COST SAVINGS

One measure of the cost savings which will result from organic acid addition at San Miguel is the change in plant operating costs in the first year of operation with a buffer in the system. Table 6-1 presents a summary of the projected 1984 (first year) cost savings for San Miguel. As shown, estimated savings in 1984 range from $271,000 for the EP-501 additive to $637,000 for the DuPont DBA additive. For the DuPont additive, the cost savings is over 3 times the projected capital expenditures giving a payback period of 4 months on the capital investment. Table 6-1 also presents a

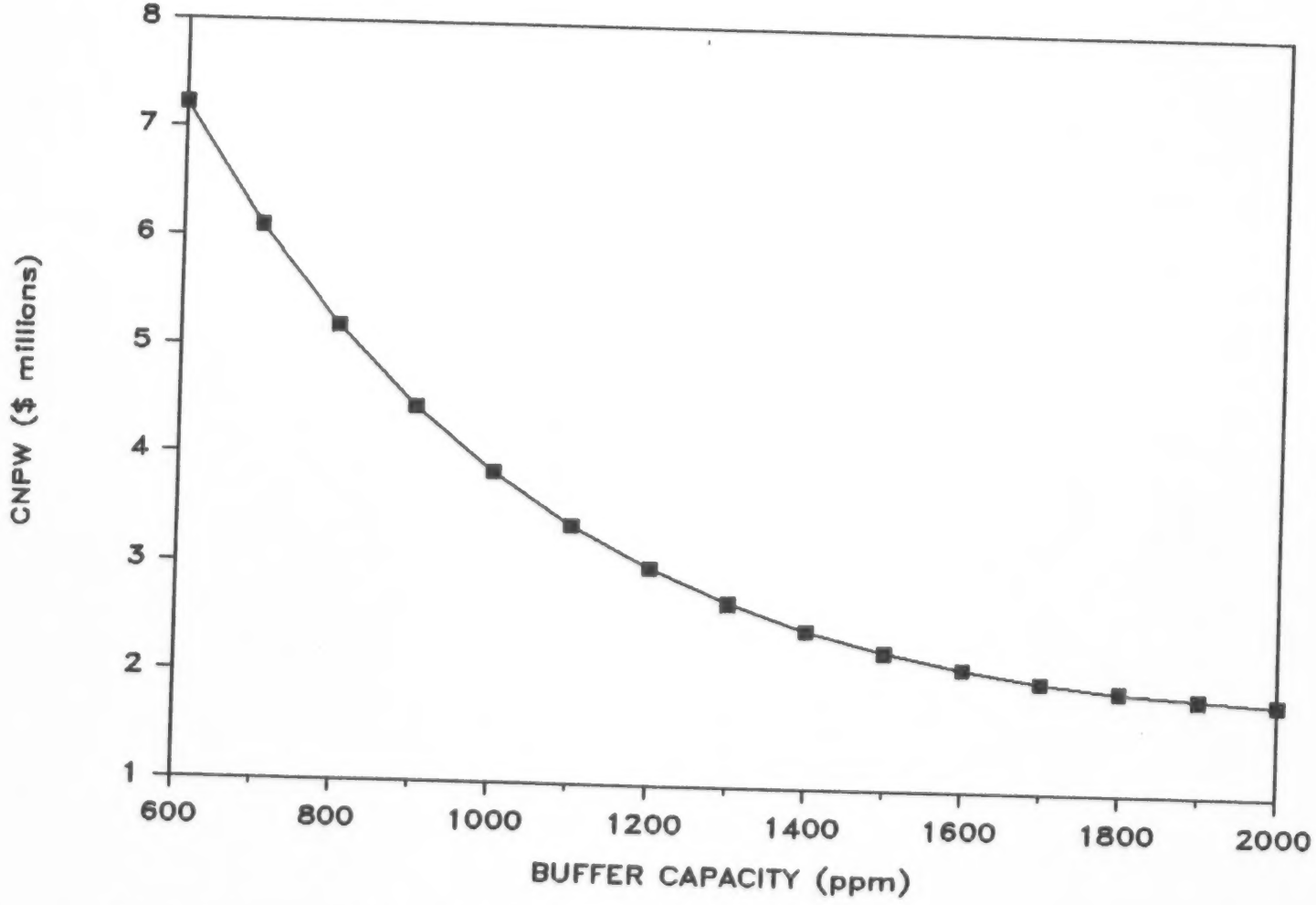

Figure 6-1. Cumulative Net Present Worth (15-year) of DuPont DBA Addition Project as a Function of Buffer Capacity.

TABLE 6-1. ESTIMATED FIRST YEAR COST SAVINGS FOR ORGANIC ACID ADDITION AT SAN MIGUEL'S UNIT 1 FGD SYSTEM

Cost Item	Estimated Savings (Cost) in $1000s Additive/Buffer Capacity		
	DuPont DBA (600 ppm)	Badische EP-306 (400 ppm)	Badische EP-501 (125 ppm)
Organic Acid	(481)	(268)	(399)
Limestone Reagent	582	499	382
Limestone Grinding	103	88	68
Sludge Disposal	212	181	139
Dewatering	28	24	18
Maintenance	63	-	-
Bypass	130	72	72
TOTAL	637	596	280

breakdown of items contributing to the overall savings. As shown, the reduction in limestone reagent consumption and associated processing costs account for the majority of the savings. The second major factor is the bypass credit and, for the DuPont DBA only, a reduction in maintenance requirements provides some additional savings. No maintenance savings are projected with use of the two Badische additives since the problems with absorber and mist eliminator pluggage were not elimniated during tests with those additives. The bases and assumptions used to develop the costs presented in Table 6-1 are detailed in Section 6.3.

6.3 CUMULATIVE NET PRESENT WORTH ANALYSIS

One method of evaluating the costs and the return on investment for a capital expenditure project is to estimate the cumulative net present worth

(CNPW) of the project. This type of analysis is especially useful when comparing two options; one which has high initial capital costs and low projected operating costs, and one which has low initial costs, but higher projected operating costs. It is also useful for comparing two options which trade-off one operating expense against another.

6.3.1 Background

A cumulative net-present worth analysis compares the costs of project options by accounting for the time value of money. It estimates what a projected savings in future dollars is worth in the dollars of a base year. In this way, a capital expense which is incurred in 1984, for example, can be compared to projected savings which will occur in 1984, 1985 and future years. The equation for calculating present worth of a cost or savings is:

$$\text{Present Worth} = \frac{\text{Cost or Savings in Future Year}}{(1 + \text{Interest Rate})^n}$$

where interest rate is expressed as a fraction and n is the number of years between the base cost year and the year the costs are estimated for. For example, for a base year of 1984, the n-value for calculating present worth of 1989 costs is 5 (i.e., 1989 - 1984). To calculate the cumulative net present worth of a project, costs or savings are projected for each year over the project life. The present worth of each year is then calculated and a total or cumulative present worth is determined by the sum of each individual year's present worth. Capital costs are included in determining the cumulative net present worth in the year in which they are incurred.

6.3.2 Results

Table 6-2 summarizes the results of three, 15-year CNPW analyses which compare the three organic acid additives tested at San Miguel. The total for each acid represents the estimated savings in 1984 dollars over a 15-year period of organic acid use in the San Miguel FGD system. As shown, the

TABLE 6-2. FIFTEEN-YEAR CUMULATIVE NET PRESENT WORTH FOR THE THREE ADDITIVES TESTED AT SAN MIGUEL

Savings/ Cost Component*	Estimated Savings (Costs) in $1000s Acid/Buffer Capacity		
	DuPont DBA/ 600 ppm	EP-306/ 460 ppm	EP-501/ 125 ppm
Capital Investment	(215)	(215)	(215)
Organic Acid	(6093)	(3395)	(5054)
Limestone Reagent	6939	5949	4562
Limestone Grinding	1306	1120	859
Sludge Disposal	2523	2163	1659
Maintenance	752	--	--
Dewatering	353	303	232
Bypass Credit	1650	914	914
TOTAL	7215	6839	2957

*All costs in mid-1984 dollars.

projected savings for the three additives range from about $3 million for the Badische EP-501 additive to $7.2 million for the DuPont DBA additive. This indicates that San Miguel will realize a very significant savings from the use of an organic acid additive. At current prices, the DuPont additive is the most attractive offering a 6 percent greater savings than the Badische EP-306 additive. Also, operation with the DuPont DBA provides additional benefits such as reduced absorber and mist eliminator pluggage and improved thickener operation. While some maintenance credit was included in the savings for the DuPont DBA, the full value of these benefits was not quantitied in the CNPW analysis. There was no estimate of increased reliability or decreased capital expenditures (e.g., lower replacement rates for the mist eliminator blades) included in the DuPont cost/savings analysis.

The only cost items included in the CNPW analysis are the capital investments associated with the organic acid addition system and the continuing costs for the organic acid additive. The capital investment shown represents the initial investment in 1983, the costs incurred for repairs due to corrosion, and planned expenditures to improve the organic acid addition system in 1984. Since most of the capital costs have already been incurred, these will not be affected by the projected CNPW. However, a significant change in the delivered price of DBA or limestone could have a proportionally significant impact (either positive or negative) on the present worth of the organic acid addition project at San Miguel. This should be considered in using the San Miguel results to evaluate organic acid addition for other applications.

Of the items in Table 6-2 which represent cost savings, most are related to the improvement in limestone utilization including:

- Limestone Reagent Cost Savings - This represents the improvement in limestone utilization which resulted from operation at lower quencher pHs. The correlation presented in Section 5 was used in conjunction with the average pHs measured during individual tests (Table 5-1) to determine limestone utilization for each organic acid. Baseline limestone consumption was estimated at 70 percent utilization (Table 5-2).

- Limestone Grinding Cost Savings - The reduction in limestone grinding costs were calculated based on the estimated reduction in annual reagent consumption, costs for electricity (Table 6-3), and the operating characteristics of the limestone grinding circuit (Table 6-4). In addition, a reduction in the quantity of balls required to maintain the ball mill charge was estimated.

- Sludge Disposal Savings - Reducing the excess limestone produces a proportional reduction in the quantity of waste sludge generated by the FGD systems. Savings associated with sludge

disposal were estimated based on the limestone savings, operating characteristics of the dewatering area, and San Miguel's costs for waste disposal.

- Dewatering Cost Savings - A reduction in the mass of waste generated also reduces the load on the vacuum filtration system. This cost savings represents the reduction in power consumption which results from reduced operating time for the dewatering system.

There are two other items not related to limestone consumption which contribute to the projected cost savings at San Miguel. These items are:

- Reduced Absorber Maintenance - As discussed in Section 5, the use of DuPont DBA at buffer capacities of 600 ppm or greater allowed the San Miguel FGD system to operate at conditions which reduced the tendency of the absorbers and mist eliminators to plug. San Miguel estimates that this has reduced the FGD system maintenance by at least half. Since contract labor was used to clean the absorbers and mist eliminators, a reduction in maintenance represents a real cost savings. The maintenance cost savings was not included for the two Badische additives. This is because at the buffer capacities these additives were tested, the FGD system operated at conditions which did result in plugging in the absorbers and mist eliminators.

- Bypass Credit - The use of organic acids in the San Miguel FGD system permitted varying amounts of flue gas to be bypassed around the modules. This hot gas was then mixed with the cool, saturated flue gas from the scrubbers and mixture then reheated with 400°F steam-heated air. The degree of air reheat required depends on the amount of bypass. Higher bypass rates result in reduced reheat requirements. At even low buffer capacities, it became possible to bypass some flue gas around the scrubber modules. This

reduced reheat steam requirement represents an energy credit with attendent cost savings which can be attributed to organic acid addition. For the DuPont tests, the amount of bypass was found to be a function of buffer capacity in the system (at constant inlet SO_2 levels). This relationship (Figure 5-5) was used to evaluate the cost savings for the DuPont DBA. For the Badische additives, bypass rates estimated at the actual test conditions were used.

The above items represent the factors which contribute to the costs and savings projected for organic acid use at San Miguel. The next subsection provides details of the unit costs, system operating characteristics, and escalation factors used in developing the CNPW analysis presented in Table 6-2.

6.3.3 Bases for CNPW Analyses

The results of the CNPW analyses are based on operating characteristics of the San Miguel power plant, FGD system performance data collected during the test program, actual costs for materials and services, and San Miguel's escalation factors for projecting future materials costs and the time value of money. As such, the results in Table 6-2 should represent savings San Miguel will realize in operation during the next 15 years.

The cost factors used in the CNPW analysis are shown in Table 6-3. The costs of organic acids and limestone represent prices are FOB the San Miguel site. The electricity costs represent a bussbar sales price and the steam cost is based on San Miguel's fuel price and the thermal efficiency of the boiler. Other costs represent actual costs for materials or services. The cost escalation factors are also San Miguel's with 8.5 percent representing a petroleum related escalation factor, 7.5 percent the non-petroleum related factor, and 11.25 percent the interest rate. The use of the petroleum and non-petroleum factors for a given material or service was selected by Radian.

TABLE 6-3. UNIT COSTS AND ESCALATION FACTORS FOR PRESENT WORTH ANALYSIS

Cost Factor	Unit	Unit Cost ($)	Escalation Factor
Raw Materials			
DuPont DBA*	lb	0.24	8.5
Badische EP-306*	lb	0.19	8.5
Badische EP-501*	lb	0.23	8.5
Limestone*	ton	11.00	7.5
Utilities			
Electricity	kwh	0.04	8.5
Steam	10^6 Btu	1.33	8.5
Equipment Cost			
Original Installation	-	133,000	11.25
Additional Improvements	-	50,000	-
Corrosion Repairs	-	15,000	11.25
Labor Cost	hr	10.00	7.5
Interest	%	-	11.25
Miscellaneous			
Coal	10^6 Btu	1.00	8.5
Mill Balls*	ton	500.00	7.5
Sludge Disposal	ton	2.00	7.5

*Prices are FOB San Miguel Plant.

Table 6-4 presents the calculational basis used in estimating annual costs and cost savings for specific unit operation in the FGD system. These numbers are, for the most part, based on actual operating levels at the San Miguel plant.

TABLE 6-4. ASSUMPTIONS AND BASES FOR PRESENT WORTH ANALYSIS

Unit Boiler		**Dewatering Plant**	
Avg. Load	410 MW	Operating Power	651 kw
Operating Time	7,200 hrs/yr	Solids Throughput	49 tons/hr
Gross Heat Rate	10,500 Btu/kwh	Filter Cake Solids	50%
Thermal Efficiency	75%		
Flue Gas		**Scrubber Mainternance Labor**	
SO_2 To Scrubbers	7.08 lbs/10^6 Btu	Annual Labor	12,600 man hrs
SO_2 Out Stack	1.10 lbs/10^6 Btu		
Stack Temp.	175°F		
Heat In Bypass	2,582 Btu/Mscf		
Reagent Preparation		**Limestone Utilization**	
Mill Motor Amps	134	Baseline	70%
Mill Motor Volts	6,900	Baseline Tonnage	206,900 tons/yr
Power Factor	0.88	**Fuel**	
Mill Throughput	46 tons/hr	Heating Value (as received)	5,650 Btu/lb
Mill Ball Consumption	2,000 lbs/day	Sulfur (as received)	2%

SECTION 7
CONCLUSIONS

This section presents conclusions based on the results of the test program conducted at San Miguel Electric Cooperative's Unit 1 FGD system. The conclusions presented are divided into 2 categories:

(1) Specific conclusions relating to the tests conducted at San Miguel, and

(2) Conclusions which generalize the results of the San Miguel test program.

Each of these areas is summarized below.

7.1 SPECIFIC CONCLUSIONS

Several specific conclusions can be drawn based on the results of the San Miguel test program:

- The use of organic acids in the San Miguel FGD system resulted in a significant improvement in process operation and a very substantial cost savings. The maximum estimated savings was over $600,000 in first year savings. This translates to $7.2 million in 1984 dollars over a 15-year period. These maximum savings were calculated for DuPont DBA additive to attain an average buffer capacity of 600 ppm.

- Savings for the Badische additive, EP-306, were only slightly lower than for the DuPont material. However, the EP-306 additive

was not "penalized" for the foaming problem, which made operation at a buffer capacity of more than 500 ppm very difficult. In fact, foaming was so severe that this test was terminated, and subsequent tests planned for higher buffer capacities were cancelled.

- Savings for the Badische additive, EP-501, were substantially less than for either the DuPont DBA or EP-306. This was due to a very high consumption rate of EP-501, relative to the buffer capacity provided.

- The key to realizing the savings associated with organic acid addition at San Miguel was a significant reduction in limestone stoichiometry in the FGD system. Limestone stoichiometry was reduced by reducing operating pHs in the quench and absorber recirculation loops.

- Another benefit of operating at a lower absorber pH was a reduction in the pluggage of absorber trays and mist eliminator passages.

- Use of organic acids at San Miguel made some flue gas bypass possible. This contributed to the projected cost savings by reducing the requirement for reheat steam.

- Organic acid concentrations were not found to have a direct effect on the limestone utlilization of the system. Only by allowing operation at lower pHs did the organic acids affect utilization.

- Tests with manganese added to the FGD system showed no effect on the organic acid consumption rate. This is in contrast to previous test results.

In conclusion, substantial benefits resulted from the use of organic acids in the San Miguel FGD system. Significant cost savings will be realized by San Miguel due to changes in FGD operating conditions made possible by organic acid use. Also, improvement in FGD operation (such as reduced absorber and mist eliminator pluggage) was an indirect result of organic acid use at San Miguel. Because of these benefits, San Miguel plans to continue organic acid addition to the FGD system.

7.2 GENERAL CONCLUSIONS

The results of the San Miguel tests can be used by other utilities who are considering the use of organic acids to their FGD system. Although the actual cost savings realized at San Miguel are site-specific, some general conclusions concerning the results are:

- FGD systems which are currently meeting SO_2 emission regulations at high limestone stoichiometries are good candidates for reducing operating costs with DBA.

- Systems which have poor limestone stoichiometries accompanied by absorber and mist eliminator plugging are also good candiates.

Care must be exercised in evaluating these situations, however. Simply adding organic acids to the FGD system will not cure all the problems. Careful consideration must be given to selecting operating conditions which will provide the maximum benefit from organic acids. Also, other areas of the FGD system (e.g., the limestone grinding circuit) may need to be optimized to receive the full benefits which can be achieved with the help of organic acids.

APPENDIX A
DATA QUALITY

This appendix presents the results of checks made on data quality during the San Miguel test program. The QC efforts for San Miguel focused on key measurements designed to address the main program objective: what was the economic impact of organic acid addition on the San Miguel FGD system. The process and anlaytical measurements which were important in answering this question were:

(1) $CaCO_3$ utilization in the FGD system,
(2 Organic acid buffer capacity in the FGD system,
(3) Organic acid addition rate to the FGD system, and
(4) SO_2 emissions from the FGD system.

The results of QC efforts in each of these areas are summarized in the following discussion.

$CaCO_3$ Utilization

$CaCO_3$ (i.e., limestone) utilization in the San Miguel FGD system was measured by analysis of grab samples from the thickener feed stream. Solids from slurry samples were analysed for $CO_3^=$ and total sulfur as $SO_4^=$. Then the $CaCO_3$ utilization was determined by the following calculation:

$$CaCO_3 \text{ utilization} = \frac{\text{moles } CaCO_3 \text{ reacted}}{\text{moles } CaCO_3 \text{ fed}} \times 100\%$$

$$= \frac{\text{moles } SO_4^= \text{ (total S)}}{\text{moles } SO_4^= + \text{moles } CO_3^=} \times 100\%$$

As part of the quality control program, QC sample analysis and replicate analyses for $CO_3^=$ and $SO_4^=$ were conducted. The results of the QC sample analyses for carbonate and sulfate are presented in Figures A-1 and A-2, respectively.

Figure A-1 presents the relative value of the carbonate replicate analysis as a function of the analysis sequence. Relative carbonate concentration is shown because three QC samples were used during the test program. The three lines in the figure represent the mean carbonate value and upper and lower 95 percent confidence intervals about the mean. As shown, all but one of the replicate analyses are within 5 percent of the mean carbonate value. This results in a relative standard deviation of 2.1 percent for the QC sample analyses. The 95 percent confidence intervals in the figure represent approximately ± 1 percent of the mean concentration.

Figure A-2 presents the results of replicate sulfate analyses as a function of analysis sequence. The number of QC analyses for sulfate is less than that for carbonate because the sulfate analyses were conducted at Radian's Austin laboratories over a short period at the end of the test program, while most of the carbonate analyses were completed on site over the duration of the program. The three lines in Figure A-2 represent the mean sulfate value and the upper and lower 95 percent confidence intervals about the mean. As shown, all but one of the replicate analyses are within 5 percent of the mean sulfate concentration. This results in a standard deviation of 0.21 mmole/l for the QC sample analyses and a CV of 4.3 percent. The 95 percent confidence intervals in the figure represent approximately ± 4 percent of the mean concentration.

A number of repeat or duplicate analyses for carbonate and sulfate were conducted on the samples used to quantify limestone reagent utilization in the San Miguel FGD system. The results of these duplicate analyses are summarized in Tables A-1 and A-2. Each table presents the original and duplicate values, the mean of the two values, and the standard deviation and

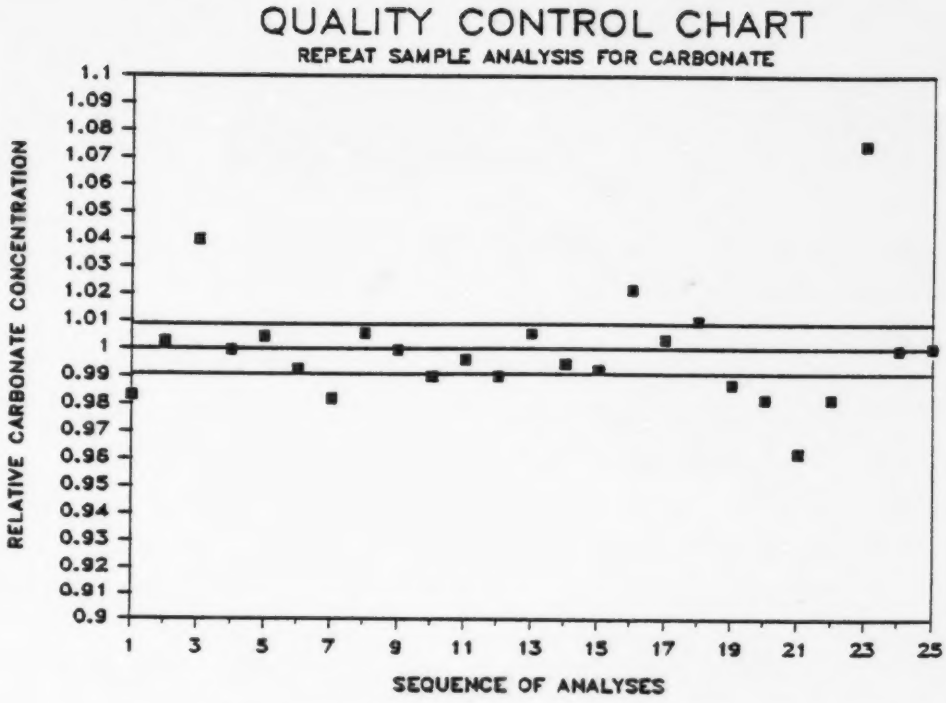

Figure A-1. Repeat Analysis for Carbonate.

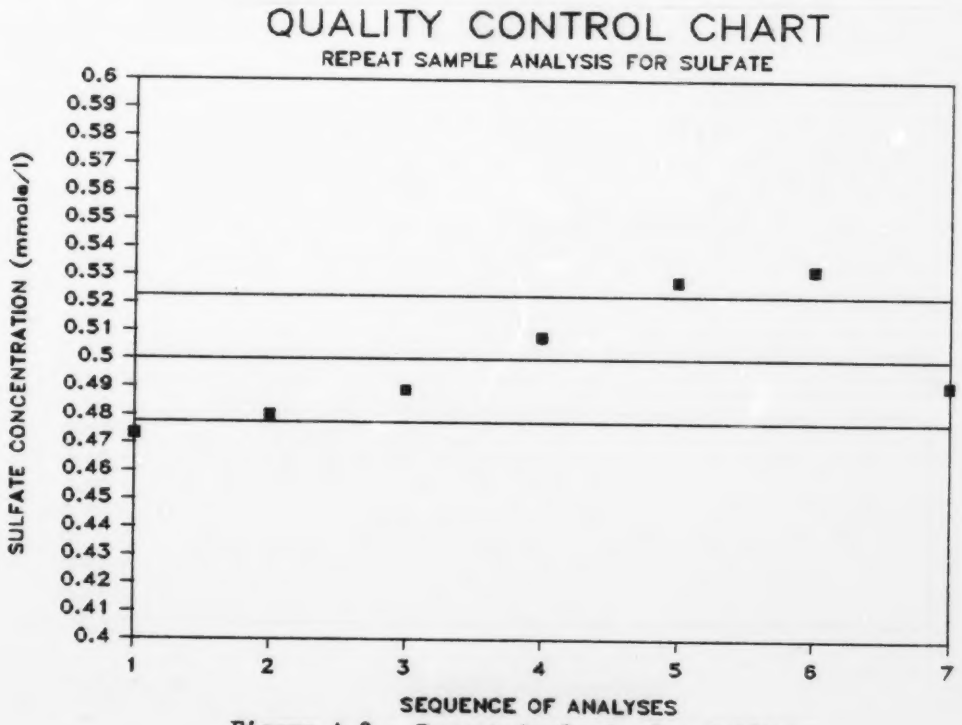

Figure A-2. Repeat Analysis for Sulfate.

TABLE A-1. CARBONATE REPLICATE ANALYSIS RESULTS

Date	Original (mmole/gm	Duplicate (mmole/gm)	Average (mmole/gm)	Standard Deviation	Coefficient of Variance
17-Nov-83	2.85	2.69	2.77	0.08	2.89
23-Nov-83	2.60	2.55	2.58	0.02	0.97
02-Dec-83	0.11	0.12	0.11	0.00	2.22
08-Dec-83	5.01	5.03	5.02	0.01	0.20
16-Dec-83	0.58	0.59	0.59	0.00	0.85
10-Jan-84	2.77	2.69	2.73	0.04	1.47
13-Jan-84	1.31	1.35	1.33	0.02	1.50
27-Jan-84	0.64	0.58	0.61	0.03	4.43
17-Apr-84	3.18	3.15	3.17	0.01	0.47
17-Apr-84	5.08	5.10	5.09	0.01	0.20
17-Apr-84	1.14	1.08	1.11	0.03	2.70
18-Apr-84	0.45	0.40	0.43	0.02	5.83
18-Apr-84	2.14	2.14	2.14	0.00	0.00
18-Apr-84	3.33	3.28	3.31	0.02	0.76
19-Apr-84	0.81	0.77	0.79	0.02	2.03
19-Apr-84	1.31	1.18	1.25	0.06	5.22
19-Apr-84	1.03	0.96	1.00	0.03	3.36
20-Apr-84	0.58	0.62	0.60	0.02	3.58
20-Apr-84	2.49	2.13	2.31	0.18	7.79
			POOLED COEFFICIENT OF VARIATION	=	3.22

TABLE A-2. SULFATE REPLICATE ANALYSIS RESULTS

Date	Original (mmole/gm	Duplicate (mmole/gm)	Average (mmole/gm)	Standard Deviation	Coefficient of Variance
23-Apr-84	0.473	0.480	0.48	>.00	0.79
23-Apr-84	0.808	0.800	0.80	>.00	0.46
23-Apr-84	0.600	0.599	0.60	>.00	0.13
24-Apr-84	0.832	0.823	0.83	>.00	0.54
24-Apr-84	0.417	0.408	0.41	>.00	1.09
24-Apr-84	0.212	0.208	0.21	>.00	0.95
24-Apr-84	0.528	0.532	0.53	>.00	0.38
			POOLED COEFFICIENT OF VARIATION	=	0.70

coefficient of variance (i.e., relative standard deviation). Overall precision for the duplicate analysis is expressed in terms of the pooled (i.e., "average") coefficient of variation, calculated as:

$$\text{pooled CV} = \left(\frac{CV_1^2 + CV_2^2 + CV_n^2}{n}\right)^{1/2}$$

The pooled CV for the duplicate analyses is a measure of the within-day analytical precision or replicability. Ten percent is typically considered to be an acceptable level of precision for replicate analyses while a CV of five percent or less is considered to be very good. The pooled VC values in Tables A-1 and A-2 of 3.2 percent for carbonate and less than 1 percent for the sulfate anlayses indicate excellent precision on these analyses.

A final check on the accuracy of the reagent utilization was made by analyzing selected solids samples for sulfite and completing solids material balances on those samples. The equation used for the material balance calculation is shown below:

$$\left[\left(\frac{\text{mmole } SO_3^=}{\text{gm}} \times \frac{1 \text{ mole } CaSO_3/CaSO_4 \text{ Solid Solution}}{.85 \text{ moles } SO_3^=} \times \frac{131.4 \text{ mg}}{\text{mmole}}\right) + \left(\frac{\text{mmole } SO_4^= \text{ (total)}}{\text{gm}} - \frac{\text{mmole } SO_3^=}{\text{gm}} \times \frac{1}{.85}\right) \times \frac{174.1 \text{ mg}}{\text{mmole}} + \left(\frac{\text{mmole } CO_3^=}{\text{gm}} \times \frac{100.1 \text{ mg}}{\text{mmole}}\right) + \text{fraction inerts}\right] \times \frac{1 \text{ gm}}{1000 \text{ mg}}$$

$$\times 100\% = \frac{(\text{gms } CaCO_3 + CaSO_3/SO_4 \cdot 1/2\ H_2O + CaSO_4 \cdot 2H_2O + \text{Inerts})\%}{\text{gm solids analyzed}}$$

This calculation determines how many grams of solids are calculated to be in 1 gram of sample based on the $CO_3^=$, $SO_4^=$ (total), and $SO_3^=$ analyses. Values ranging from 95 to 105 percent are considered good.

Table A-3 presents the results of solids material balance calculations for the San Miguel solids samples. As shown, the average material balance based on chemical analysis accounted for 98 percent of the solids sample with a standard deviation of 2.2 percent. This is excellent agreement, especially considering the fact that the material balance incorporates an assumption concerning the composition of the $CaSO_3/CaSO_4$ solid solution.

Organic Acid Buffer Capacity

Aside from limestone utilization, the other major variable of interest in the San Miguel FGD system which was quantified by chemical analysis was organic acid buffer capacity. As with $CO_3^=$ and $SO_4^=$, both QC samples and replicate analyses were used to insure the accuracy of the buffer capacity measurement.

Figure A-3 presents replicate buffer capacity analyses as a function of analysis sequence. The three lines in the figure represent the mean buffer capacity value and upper and lower 95 percent confidence intervals about the mean. As shown, the majority of the replicate analyses are within 10 percent of the average. This results in a relative standard deviation (CV) of approximately 10 percent which is considered adequate for buffer capacity analyses. The greater deviation in these analyses (relative to the carbonate and sulfate analyses) is probably a result of variations of the background buffer capacity in the samples, a value which cannot easily be characterized. Although the standard deviation of these analyses is 10 percent, the results are suitable accuracy for the San Miguel characterization tests.

Table A-4 presents the results of duplicate analyses for buffer capacity. The accuracy of these values is important to the interpretation of the San Miguel data since relative buffer capacities were used in calculating accumulation rates in the FGD system. As shown in Table A-4, most of the duplicate analyses have coefficients of variation of less than 1 percent and only 1 replicate has a CV of greater than 5 percent. This results in a

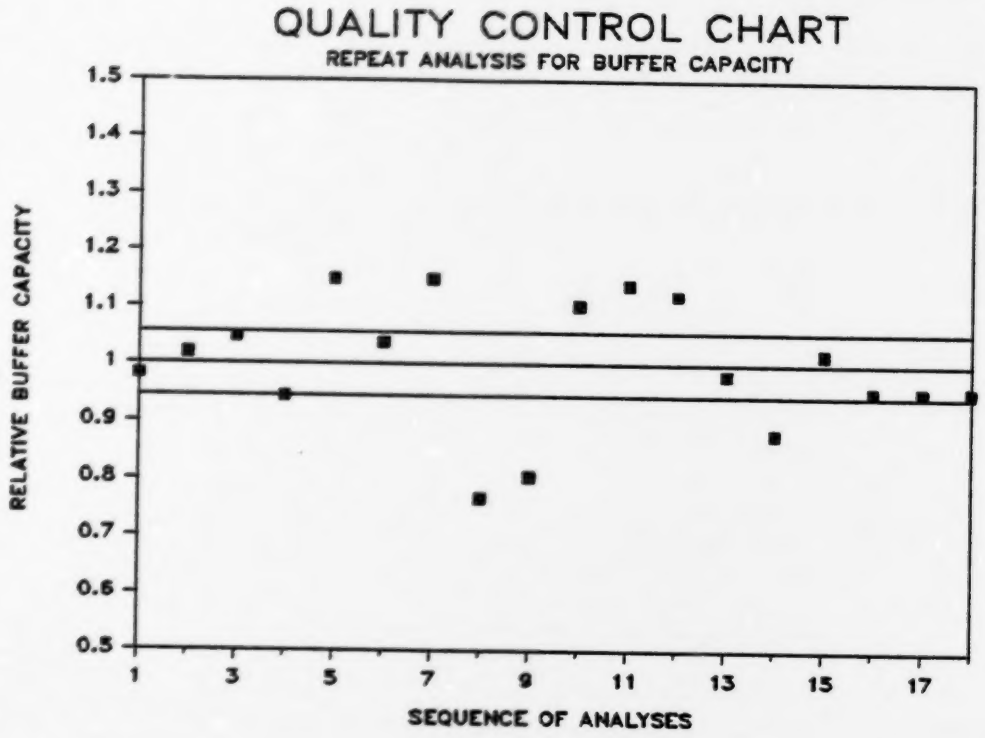

Figure A-3. Repeat Analysis for Buffer Capacity.

TABLE A-3. SAN MIGUEL SOLIDS MATERIAL BALANCES

Sample ID	$SO_3^=$ mmol/g	$SO_3^=$ mmol/g	$SO_4^=$ mmol/g	Inerts %	Closure %
SM-014	2.9	4.0	5.1	2.3	98.2
SM-015	2.8	4.2	5.1	2.4	96.8
SM-016	3.2	4.0	4.9	2.3	98.3
SM-017	2.4	4.4	5.4	2.3	96.7
SM-018	1.8	4.8	6.0	2.3	100.0
SM-019	1.8	4.8	6.0	2.3	99.1
SM-092	1.4	4.7	6.2	1.8	97.7
SM-093	5.0	2.8	3.6	2.2	99.5
SM-094	0.8	5.0	6.7	2.0	98.3
SM-095	0.2	5.2	7.0	2.0	96.1
SM-096	1.0	4.8	6.3	2.0	94.0
SM-122	1.4	5.0	6.7	2.5	104.5
SM-123	0.2	5.4	7.1	2.1	97.3
SM-124	1.1	5.0	6.5	2.3	99.1
SM-125	0.2	5.4	7.2	2.3	98.3
SM-126	0.6	4.8	6.6	2.3	95.6
SM-127	0.1	5.1	7.1	2.3	96.3
SM-166	2.0	4.4	5.7	2.2	97.1
SM-167	0.8	5.3	6.5	2.4	96.8
SM-168	1.9	4.3	5.8	2.3	97.8
SM-169	0.5	5.3	7.0	2.3	98.6
SM-170	2.1	4.2	5.9	2.3	100.8
SM-171	0.7	5.1	6.6	2.3	95.8
SM-230	2.1	4.2	5.6	2.9	97.6
SM-231	1.4	4.7	6.1	2.7	97.6
SM-234	3.5	3.5	4.6	2.8	97.9
SM-235	2.9	3.9	5.1	2.8	99.1
SM-284	1.2	4.9	6.4	3.0	99.5
SM-285	0.8	5.0	6.7	2.9	99.2
SM-286	1.3	4.5	6.1	2.9	97.0
SM-287	0.9	4.8	6.4	2.9	96.1
SM-288	0.8	4.6	6.3	2.9	93.8
SM-289	1.4	4.9	6.6	2.9	103.3
		AVERAGE MATERIAL BALANCE RESULT =			98.0
		STANDARD DEVIATION =			2.2

TABLE A-4. BUFFER CAPACITY REPLICATE ANALYSES

Date	Original (ppm)	Duplicate (ppm)	Average (ppm)	Standard Deviation	Coefficient of Variation
21-Nov-83	690	690	690	0.00	0.00
21-Nov-83	700	730	715	15.00	2.10
22-Nov-83	430	413	421.5	8.50	2.02
29-Nov-83	548	550	549	1.00	0.18
30-Nov-83	755	748	751.5	3.50	0.47
02-Dec-83	306	312	309	3.00	0.97
07-Dec-83	938	923	930.5	7.50	0.81
07-Dec-83	806	811	808.5	2.50	0.31
08-Dec-83	1350	1344	1347	3.00	0.22
08-Dec-83	836	820	828	8.00	0.97
14-Dec-83	1098	1097	1097.5	0.50	0.05
14-Dec-83	1494	1504	1499	5.00	0.33
15-Dec-83	1400	1400	1400	0.00	0.00
15-Dec-83	1349	1350	1349.5	0.50	0.04
16-Dec-83	2316	2320	2318	2.00	0.09
20-Dec-83	1809	1796	1802.5	6.50	0.36
20-Dec-83	1261	1263	1262	1.00	0.08
22-Dec-83	2567	2637	2602	35.00	1.35
23-Dec-83	1817	1824	1820.5	3.50	0.19
09-Jan-84	1095	1074	1084.5	10.50	0.97
09-Jan-84	547	562	554 5	7.50	1.35
09-Jan-84	18.7	18.6	18.65	0.05	0.27
13-Jan-84	19.4	19.3	19.35	0.05	0.26
13-Jan-84	595	589	592	3.00	0.51
17-Jan-84	665	656	660.5	4.50	0.68
17-Jan-84	556	555	555.5	0.50	0.09
25-Jan-84	448	450	449	1.00	0.22
25-Jan-84	10.2	12.5	11.35	1.15	10.13
26-Jan-84	880	884	882	2.00	0.23
26-Jan-84	707	713	710	3.00	0.42
27-Jan-84	441.5	431.9	436.7	4.80	1.10
13-Mar-84	1028	1035	1031.5	3.50	0.34
14-Mar-84	919	943	931	12.00	1.29
15-Mar-84	1241	1155	1198	43.00	3.59
16-Mar-84	1513	1556	1534.5	21.50	1.40
16-Mar-84	1244	1165	1204.5	39.50	3.28
		POOLED COEFFICIENT OF VARIATION =			2.03

pooled CV for the buffer capacity titration of 2 percent which represents excellent precision for this analysis.

Organic Acid Addition Rate

Organic acid addition to the FGD system was monitored by a number of manually adjusted glass tube rotameters which were used to meter acid into the system. These rotameters were set with the desired feed rate and plant operators checked, recorded, and adjusted the feed rate setpoint once an hour, 24 hours a day. The rotameter setpoints were found to be very stable and they did not drift significantly (more than 5 percent) from hour to hour. This stability is attributed to the use of a positive displacement pump for organic acid feed.

To insure the accuracy of the organic acid addition rate, the rotameters used to monitor organic acid addition were calibrated at the beginning and end of the test program. In addition, the integrated acid addition rate was compared with the drop in the acid tank level where possible.

Table A-5 presents the results of the rotameter calibration checks made during the San Miguel test program. As shown at the start and end of the test program, the setpoint of the active rotameters had less than a 5 percent deviation from the measured flow rate, which is considered very good agreement. The deviation between actual and measured probably represents the accuracy of the measurement technique (graduated cylinder and stopwatch) rather than any actual deviation on the part of the rotameters.

As mentioned earlier, the organic acid feed rate was checked during the test program by comparing the measured feed tank level drop with the integrated organic acid feed rate. The results of three such comparisons are presented in Table A-6. As shown, the tank level drop measurement agrees well with the integrated flow rate measured by the rotameters. These data indicate that the rotameters provided an accurate measure of organic acid flow during the San Miguel test program.

TABLE A-5. ORGANIC ACID ROTAMETER CALIBRATION CHECK

Time	Setting	Measured Flow*	Relative** Accuracy (%)
Test Start	0.5 gpm	0.5	0%
Test Start	1.0 gpm	1.05	-4.8%
Test Start	1.5 gpm	1.54	-2.6%
Test End	1.0 gpm	0.96	+4.2%

*Average of active flowmeters, 3 readings each

**RA = (setpoint - measured)/(measured) x 100%

TABLE A-6. MEASURED TANK DROP VS INTEGRATED FLOW RATE

Tank Drop (gal)	Integrated Flow (gal)	Relative* Accuracy (%)
10,600	10,320	-2.6%
6,300	6,120	-2.9%
6,480	6,100	-5.9%

*RA = (Integrated Flow-Tank Drop)/(Tank Drop) x 100%

measure of organic acid flow during the San Miguel test program.

System SO_2 Emissions

System SO_2 emissions were monitored by San Miguel using an extractive stack CEMS consisting of a TECO pulsed florecence SO_2 analyzer and a Horiba CO_2 analyzer. This CEMS system was calibrated and spanned every weekday during the organic acid test program. If problems with accuracy and/or dirft were encountered, the San Miguel instrument engineer would take corrective action and the stack monitor was never inoperative for more than a shift.

In addition to San Miguel's efforts to maintain their CEMS, EPA under a separate program had the CEMS subjected to certification procedures during the organic acid addition test. The certification tests were conducted by Entropy Environmentalists, Inc. as part of another EPA project. Because of these superior efforts to certify and maintain the stack monitor at San Miguel, Radian made no additional QC effort for the CEMS.

APPENDIX B

CONVERSION FACTORS

To Obtain	Multiply	By
l	gal.	3.785
M^3/sec	10^3 ft^3/min	0.4719
l/s	gal./min	0.06308
kg	lb	0.4536
kg/l	lb/gal.	0.1198
metric tons	tons (short)	0.9072
g-mole	lb-mole	453.6
kW	hp	0.7457
Pascals	psia	6895
ng/J	lb/10^6 Btu	430
°C	°F-32	0.5556
J/kg	Btu/lb	2326
M	ft	0.3048
J	Btu	1055.1